European Commission

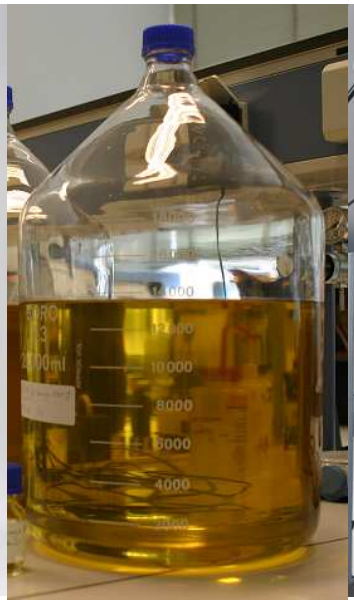
JRC SCIENTIFIC AND POLICY REPORTS

# Report on the 13th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

## Four marker PAHs in spiked olive oil

**Stefanka Bratinova, Zuzana Zelinkova, Lubomir Karasek and Thomas Wenzl**

2013


Joint Research Centre

Report EUR 26401 EN

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

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JRC 87021

EUR 26401 EN

ISBN 978-92-79-34940-9

ISSN 1831-9424

doi:10.2787/84377

Luxembourg: Publications Office of the European Union, 2013



Printed in Belgium

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

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## Four marker PAHs in spiked olive oil

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EC-JRC-IRMM
(December 2013)

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# 1. Executive summary

The EU and national reference laboratories, as designated in European Union food safety legislation, should contribute to a high quality and uniformity of analytical results. This objective can be achieved by activities such as the use of validated analytical methods, ensuring that reference materials are available, the organisation of comparative testing and the training of laboratory staff.

This report presents the results of the thirteenth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAHs) as a proficiency test (PT) on the determination of the four EU marker PAHs, benz[*a*]anthracene (BAA), benzo[*a*]pyrene (BAP), benzo[*b*]fluoranthene (BBF) and chrysene (CHR), in olive oil. It was conducted in accordance with ISO Standard 17043 and the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.

In agreement with National Reference Laboratories (NRLs), the test material used in this exercise was commercial olive oil spiked with the 4 EU markers PAHs.

Both officially nominated NRLs and official food control laboratories of the EU Member States were admitted as participants.

Participants were free to choose the method of analysis. The 4 EU marker PAHs were chosen as target analytes since limits for their sum were recently introduced in EU legislation for contaminants in food. The performance of the participating laboratories in the determination of the target PAHs in olive oil was expressed by both z-scores and zeta-scores. Those scores provide a normalised performance evaluation to make PT results comparable. Laboratories complying with the PT scheme's fitness for purpose criterion will commonly produce scores falling between - 2 and 2. The assigned values and their associated expanded uncertainty were determined from in-house measurements at the EURL PAH applying bracketing calibration, conducted on two different days. The values obtained were in good agreement with the concentrations of the gravimetrical preparation, corrected for the purity of the reference materials and the content of the PAHs measured in blank oil.

Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with known PAH content for the verification of their instrument calibration.

This proficiency test has demonstrated the high competence of all participating laboratories in the analysis of regulated PAHs in an oil matrix. Ninety one % of the reported test results were graded with z-scores that were less than an absolute value of 2, indicating good agreement between the assigned reference values of the test material and the results reported by the participants.

For the first time EURL asked participants (NRLs and official control laboratories) to assess the compliance of the sample according to the legislative limits

# 2. Introduction

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate General Joint Research Centre hosts the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (EURL PAH). One of its core tasks is to organise inter-laboratory comparisons (ILCs) for the National Reference Laboratories (NRLs) [1, 2].

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found in the environment. In food, PAHs may be formed during industrial food processing and domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling.

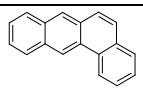
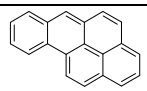
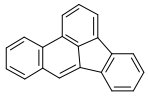
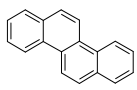
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU marker PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene (BAP) as a marker for the "total-PAH content" [3]. The toxicological importance of these compounds was confirmed in October 2005 by the International Agency for Research on Cancer (IARC), which classified BAP as carcinogen to human beings (IARC group 1), cyclopenta[*cd*]pyrene - CPP, dibenzo[*a,h*]anthracene - DHA, and dibenzo[*a,l*]pyrene - DLP as probably carcinogenic to human beings (group 2a), and nine other EU markers PAHs as possibly carcinogenic to human beings (group 2b) [4].

As a consequence, the European Commission (EC) issued Commission Regulation (EC) No 1881/2006 setting maximum levels of benzo[*a*]pyrene in food, Commission Regulation (EC) No 333/2007 laying down sampling methods and performance criteria for methods of analysis for the official control of benzo[*a*]pyrene levels in foodstuffs, and Commission Recommendation 2005/108/EC on the further investigation into the levels of PAHs in certain foods [5, 6, 7].

To evaluate the suitability of BaP as a marker for occurrence and toxicity of PAHs in food, the European Commission asked the European Food Safety Authority (EFSA) for a review of the previous risk assessment on PAHs carried out by the Scientific Committee on Food (SCF).

The scientific opinion on polycyclic aromatic hydrocarbons in food was published by EFSA in June 2008 [8]. EFSA concluded that benzo[*a*]pyrene was not a suitable indicator for the occurrence of PAHs in food and that four (PAH4) or eight (PAH8) PAHs were more suitable indicators for the total level of PAHs in food. However, PAH8 does not provide much added value compared to PAH4. Following these conclusions the Standing Committee on the Food Chain and Animal Health agreed to base risk management measures on four PAHs (PAH4) - BAA, BAP, BBF, and CHR. However, maximum levels for BAP would be maintained to ensure comparability with historical data. In the following the PAH4 will be also indicated as "the four EU marker PAHs". They are listed in Table 1**.** A maximum level for the sum of the four PAHs was included in the amendment of Commission Regulation (EC) No 1881/2006 [6]. Coherently, also Commission Regulation (EC) No 333/2007 [7] which lays down minimum method performance criteria was revised by Commission Regulation (EC) No 836/2011.

**Table 1**: Names and structures of the four EU marker PAHs.

| | | | | | |
|---|---|---|---|---|---|
| **1** | **Benz[*a*]anthracene (BAA)** |  | **2** | **Benzo[*a*]pyrene (BAP)** |  |
| **3** | **Benzo[*b*]fluoranthene (BBF)** |  | **4** | **Chrysene (CHR)** |  |

# 3. Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [2], one of the core duties of EURLs is to organise inter-laboratory comparison tests (ILCs).

This inter-laboratory comparison study aimed to evaluate the measurement capabilities of the NRLs and EU official food control laboratories (OCLs) for the 4 EU marker PAHs in olive oil. The appropriateness of the reported measurement uncertainty was also tested as this parameter is important in the compliance assessment of food with EU maximum levels.

The ILC was designed and evaluated according to ISO Standard 17043:2010. [9].

# 4. Participating Laboratories

Officially nominated NRLs and OCLs of the EU Member States were admitted as participants. The participants are listed in Table 2 and Table 3 respectively.

**Table 2: List of participating National Reference Laboratories**

| | ***Country*** |
|---|---|
| AGES GmbH | AUSTRIA |
| Scientific Institute of Public Health | BELGIUM |
| SGL - State General Laboratory, Environmental and Food Contamination Laboratory | CYPRUS |
| State Veterinary Institute Prague | CZECH REPUBLIC |
| National Food Institue, Technical University of Denmark | DENMARK |
| Danish Food and Vet. Administration in Aarhus | DENMARK |
| Tartu Laboratory of Health Protection Inspectorate Health Board | ESTONIA |
| EVIRA - Finnish Food Safety Authority Evira | FINLAND |
| ONIRIS - LABERCA | FRANCE |
| Bundesamt für Verbraucherschutz und Lebensmittelsicherheit | GERMANY |
| GCSL - General Chemical State Laboratory - Food Division - Laboratory | GREECE |
| National Food Chain Safety Office Food and Feed Safety Directorate - Food | HUNGARY |
| National Food Chain Safety Office, Food and Feed Safety Directorate - Feed | HUNGARY |
| Dublin Public Analyst Laboratory | IRELAND |
| Istituto Superiore di sanità | ITALY |
| Institute of Food Safety, Animal Health and Environment | LATVIA |
| National Food and Veterinary Risk Assessment institute | LITHUANIA |
| National Health Laboratory of Luxembourg | LUXEMBOURG |
| RIKILT- Institute of Food Safety | NETHERLANDS |
| NIFES - National Institute of Nutrition and Seafood Research | NORWAY |
| National Institute of Public Health - National Institute of Hygiene | POLAND |
| State Veterinary and Food Instute Dolny Kubin | SLOVAKIA |
| Zavod za zdravstveno varstvo Maribor | SLOVENIA |
| National Center for Food (Spanish Food Safety and Nutrition Agency) | SPAIN |
| National Food Agency | SWEDEN |
| FERA - The Food and Environment Research Agency | UNITED KINGDOM |

All participating NRL's submitted results.

**Table 3: List of participating Official Food Control Laboratories**

| *Institute* | *Country* |
|---|---|
| G.V. CONSELLERIA DE SANIDAD. Centro de Salud pública | SPAIN |
| LUFA-ITL GmbH | GERMANY |
| Food & Consumer Products Safety Authority | NETHERLANDS |
| Nofalab | NETHERLANDS |
| ASL MILANO | ITALY |
| Chemisches Untersuchungsamt Hagen | GERMANY |
| Berlin-Brandenburg State Laboratory | GERMANY |
| CVUA-MEL | GERMANY |
| Institut Dr. Wagner | AUSTRIA |
| Institut für Umwelt und Lebensmittelsicherheit | AUSTRIA |

All participating OCLs submitted results.

# 5. Time frame

The design of the ILC was agreed upon with the NRLs at the EURL PAH workshop in Prague on 14-15$^{th}$ of May 2013. It was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on the 28$^{th}$ of May 2013 (see ANNEX 2). Test samples were dispatched (see ANNEX 3) on the 9$^{th}$ of July 2013 and the deadline for reporting of results was set to the 9$^{th}$ of September 2013.

Documents sent to participants are presented in ANNEX 4.

# 6. Confidentiality

The Lab codes of participants were disclosed only to the participants, unless they were enrolled in the study by a third party, covering the participation fee. In this case the Lab codes of the respective were disclosed to the enrolling third party. In all other cases Lab codes will only be disclosed on a request and upon the written consent of the participant.

# 7. Test materials

## 7.1 Preparation

The test item of this PT was olive oil spiked with the 4 EU marker PAHs. This matrix represents the food category 6.1.1 "Oils and fats, intended for direct human consumption or use as an ingredient in food" specified in Commission Regulation (EC) No 835/2011, with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM) of 2.0 µg/kg and 10.0 µg/kg, respectively.

Participants also received a solution of the 4 EU marker PAHs in either acetonitrile or toluene (according to their choice, see ANNEX 3) with disclosed concentrations, which allowed them to check their instrument calibration against an independent reference. The technical specifications are provided in Annex 5.

The test material was prepared by the EURL PAH from three litres of olive oil, containing only a minimum amount of PAHs prior to the test item preparation. It was spiked with a PAH standard solution containing the 4 EU marker PAHs. The standard solution was prepared from neat certified

reference materials (BCR®), purchased from Institute for Reference Materials and Measurements, Geel, Belgium. Single standard stock solutions of each analyte were produced by substitution weighing of neat substance on a microbalance and dissolution in toluene. These standard stock solutions were mixed and gravimetrically diluted with toluene to obtain the solution used for spiking the olive oil. After spiking, the test sample was homogenised over night by intensive stirring. Aliquots of about 20 g spiked olive oil test material were flame sealed under inert atmosphere in 25 ml amber glass ampoules.

## 7.2 Homogeneity and stability

Homogeneity of the test item was evaluated according to ISO 13528 [11] with a test for sufficient homogeneity. A test for significant inhomogeneity was performed as well according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [12]. Ten ampoules of the test item were selected randomly and analysed by size-exclusion chromatography and solid phase extraction clean-up and gas-chromatography with mass-spectrometric detection [13]. The method precision complies with the requirements laid down in ISO 13528 [11]. The test material was rated sufficiently homogeneous for all the analytes (see ANNEX 6).

The stability of the test materials was evaluated by analysing the test material after the deadline for reporting of results. Significant differences of the analyte contents between the analysis results and the assigned value were not found (see ANNEX 6). Hence stability of the samples over the whole study period was assumed.

## 7.3 Assigned value and standard deviation for proficiency assessment

The assigned values and their associated uncertainty were determined from in-house measurements at the EURL PAH applying bracketing calibration, conducted on two different days. The obtained values were in good agreement with the gravimetrical preparation concentrations, corrected for the purity of the reference materials and the content of the PAHs measured in blank oil. The assigned values of the target PAHs are listed in Table 4.

For the individual analytes the uncertainties associated to the assigned values are equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of the test material (Table 4). The uncertainty from homogeneity and stability studies, were not significant and were not taken into consideration.

The sum of PAH4 was calculated from the individually assigned values, and the corresponding uncertainty from the uncertainties of the assigned values according to equation 1

Equation 1 $$u_{sum} = \sqrt{u_{BAA}^2 + u_{BAP}^2 + u_{BBF}^2 + u_{CHR}^2} \quad [10]$$

where $u_{sum}$ refers to the standard uncertainty of the sum of the four PAHs and
$u_{BAA}$, $u_{BAP,}$ $u_{BBF}$, and $u_{CHR}$ refer to the standard uncertainty of the individual analytes

The standard deviation for proficiency assessment, $\sigma_P$, was set for the individual analyte equal to the maximum tolerable uncertainty (Uf), which is calculated according to Equation 2. A LOD value of 0.30 µg/kg, and $\alpha$ equal to 0.2 were applied for this purpose [7]. The standard deviation for proficiency testing was calculated for the SUM parameter from the $\sigma_P$ - values of the individual analytes applying the law of uncertainty propagation.

Equation 2 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$ [7]

where $U_f$ relates to the maximum tolerated standard measurement uncertainty, LOD to the limit of detection, α to a numeric factor depending on the concentration C as given in Commission Regulation (EC) No 836/2011.

**Table 4: Analyte contents of the olive oil test material**

| | Spiking levels | Blank* | Assigned value | U | $\sigma_P$ | |
|---|---|---|---|---|---|---|
| **Analyte** | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | % |
| BAA | 3.7 | 0.3 | 3.91 | 0.14 | 0.80 | 20.4 |
| BAP | 1.5 | 0.8 | 2.97 | 0.34 | 0.61 | 20.6 |
| BBF | 1.6 | 0.2 | 1.71 | 0.27 | 0.37 | 21.8 |
| CHR | 2.8 | - | 2.46 | 0.22 | 0.51 | 20.9 |
| SUM | 9.6 | | 11.06 | 0.50 | 1.19 | 10.8 |

$\sigma_p$ standard deviation for proficiency assessment.
U expanded uncertainty of the assigned value (k=2). For the individual analytes the standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of the test material; for the SUM, the standard uncertainty is equal to the combined standard uncertainty of the four analytes (equation 1).
* The values are in the range of LODs and are only indicative for the presence of the analytes in the blank

# 8. Design of the proficiency test

The design of the PT foresaw triplicate analyses of the test sample and reporting of the individual results of replicate analyses for the single analyte. Additionally, a "value for proficiency assessment" was requested for both the single analytes and the sum of the four PAHs. All results had to be reported corrected for recovery (and recovery had to be stated in the questionnaire together with other parameters of the method applied). The "value for proficiency assessment" had also to be accompanied by the respective expanded measurement uncertainty (with a coverage factor of 2).

Participants were asked to report besides analysis results also details of the applied analysis method (see ANNEX 7).

Each participant received at least one ampoule of a solution of the target PAHs in the chosen solvent (2 ml), with disclosed content, and at least one ampoule of OIL (20 g).

# 9. Evaluation of Laboratories

## 9.1 General

The results reported by participants are listed in ANNEX 8. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed (see the Outline in ANNEX 4).

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the olive oil test material, which was expressed by z-scores, zeta-scores were calculated as well considering the uncertainty of the test results as estimated by each participant.

## 9.2 Evaluation criteria

### z-Scores

z-Scores were calculated based on the "final value". Equation 3 presents the formula for calculation of z-scores.

Equation 3 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P} \quad [11]$$

where z refers to the z-score, $x_{lab}$ to the reported "final value", $X_{assigned}$ to the assigned value, and $\sigma_P$ to the standard deviation for proficiency assessment.

### zeta-Scores

In addition to z-scores, zeta-scores were calculated. In contrast to z-scores, zeta-scores describe the agreement of the reported result with the assigned value within the respective uncertainties. zeta-Scores were calculated according to Equation 4.

Equation 4 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}} \quad [11]$$

where *zeta* refers to the zeta-score, $x_{lab}$ to the reported "final value", $X_{assigned}$ to the assigned value, $u_{lab}$ to the standard measurement uncertainty of the reported result, and $u_{assigned}$ to the standard uncertainty of the assigned value.

Whenever uncertainty was not reported by the laboratory, the corresponding zeta-score was not calculated.

Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. On the contrary, satisfactory zeta scores might be obtained even with high bias if the uncertainty is high. However, legislation specifies maximum tolerable standard uncertainties. Uncertainties exceeding them are not considered fit-for-purpose. Therefore, the uncertainties reported by the participants for the four PAHs were checked whether they comply with the thresholds provided by the "fitness-for-purpose" function (Equation 2). The results reported by the participants and the maximum tolerated LOD of 0.30 µg/kg were applied for the calculation of respective threshold values. For the SUM parameter the agreement between reported standard measurement uncertainties and the combined standard uncertainty of the 4 EU marker PAHs was evaluated. The latter was derived via the law of error propagation from the uncertainties reported for the individual analytes. Non-compliant reported uncertainties are highlighted in Table 5 and Table 6.

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [10]. The following scheme is applied for the interpretation of zeta scores and z-scores:

$|score| \leq 2.0$ = satisfactory performance
$2.0 < |score| < 3.0$ = questionable performance
$|score| \geq 3.0$ = unsatisfactory performance

## 9.3 Evaluation of results

Participants were requested to report for the four analytes, covered in this PT, the results of three replicate measurements and a "value for proficiency assessment", which is the result they wish to be applied for the calculation of performance indicators. z-Scores and zeta-scores were attributed only to these results. The individual results of replicate analyses were not rated.

Each laboratory had to report a total of 17 results (12 results for replicate measurements plus 5 values for proficiency assessment), and all 612 results have been submitted by the participants.

Statistical evaluation of the results was performed using PROLab software. Robust mean values and robust standard deviations were calculated according to Algorithm A+S of ISO 13528:2005 [11].

It should be noted that the assigned values for all measurands correspond with the robust means calculated from the participants' results (ANNEX 8). Robust standard deviations of the PT for BaA and BaP are significantly lower than target standard deviations, while for CHR the robust SD is much higher than the target level, which is coherent with the dispersion of results, observed in the previous years.

About 94 % and 88 % of the results reported from NRLs and OCLs respectively obtained a satisfactory z-score.

In Figures 1 and 2 overviews of the z-scores assigned to the results are given for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Red triangles indicate z-scores above an absolute value of three, whereas yellow triangles represent z-scores in the questionable performance range. For questionable and unsatisfactory scores, the corresponding score values are presented next to the triangles. There is one non-satisfactory result reported by a NRL, and another one reported by an OCL, both unsatisfactory results concerns determination of CHR in oil. The questionable results are in total 7.

The numerical values of the calculated z-scores are compiled in Table 5 for NRLs and OCLs. z-scores with an absolute value of above 2 are highlighted in red.

Table 6 presents the respective zeta-scores. As for the z-scores, data outside the satisfactory performance range are highlighted in red. The assessment of the performance of the participants based on the reported measurement uncertainty gave a less favourable picture. 85% for NRLs and OCLs of the zeta-scores calculated for the four individual analytes and the SUM are within the range given by $|\text{zeta}| \leq 2$. It has to be noted that the absolute value of the zeta-scores were for many participants much higher than the z-scores attributed to the same results. Consequently the laboratories perform according to internationally agreed standards, which form the basis for the z-scores, but seem to have partially difficulties in estimating realistic measurement uncertainty values although improvement could be registered from last year (75% successful zeta-score). The establishment of proper measurement uncertainty values caused problems especially for the SUM parameter. The majority of participants reported for this parameter measurement uncertainty values much higher than the value which is derived by the law of uncertainty propagation.

Hence the EURL PAHs will continue to pay special attention to this parameter, in the ILCs to come as it has major implications on the assessment of compliance of food with European legislation.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 8 together with the results of replicate analyses and Kernel density plots. Data are presented as reported by the participants.

For each analyte the figure shows the individual analysis results of the three replicate determinations. The assigned value is shown as dotted line. The blue bars represent the expanded uncertainties reported by participants for the "value for proficiency assessment". The arithmetic mean of the results of the individual participant is indicated in the blue bar by a blue line. The limits of tolerance represent deviations from the assigned value of $\pm 2\sigma_{p.}$

As could be seen from the Kernel density plots the distribution of results for each analyte and for the sum of the analytes were close to a Gaussian distribution. The robust mean and the major mode are very close to the assigned (reference) value, which demonstrates that there is no method dependant bias.

**Figure 1:** Graphical presentation of z-scores corresponding to the "final values" reported by the **NRLs** for the contents of BAA, BAP, BBF, CHR, and the SUM parameters in the spiked olive oil test material.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the questionable and non-satisfactory results.

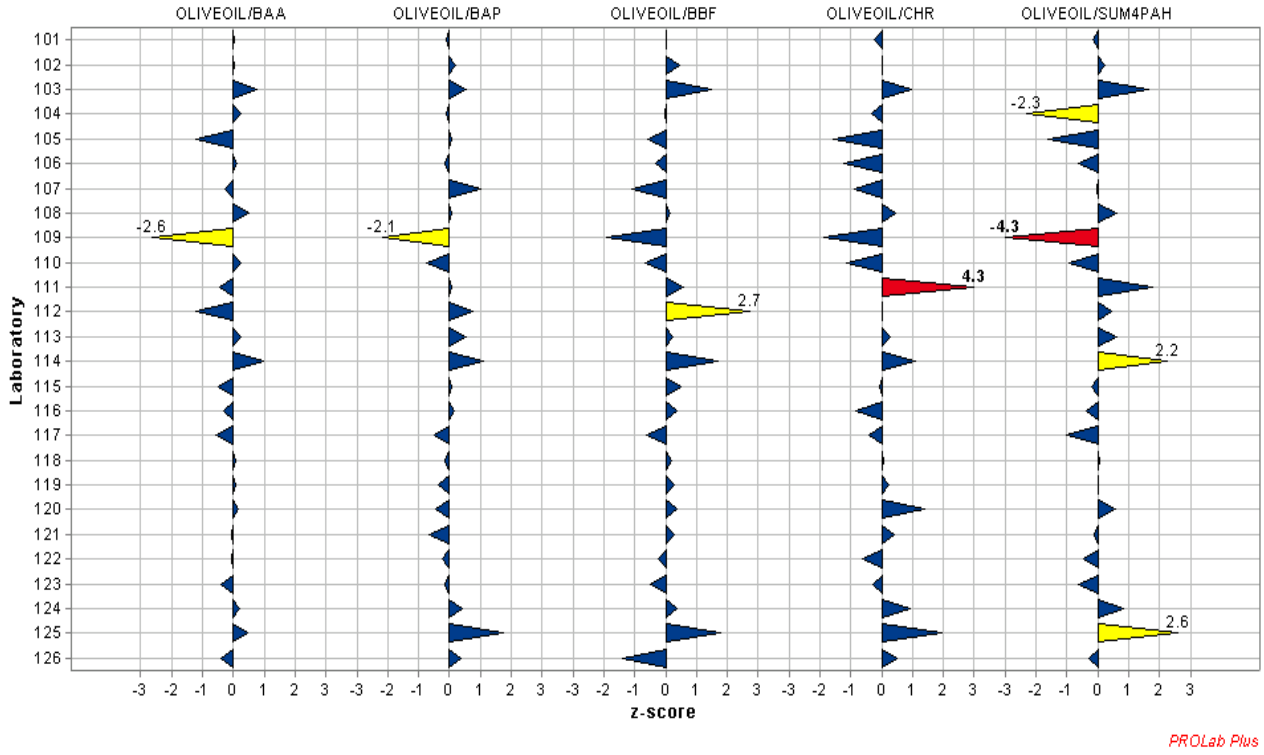



**Figure 2:** Graphical presentation of z-scores corresponding to the "final values" reported by the **OCLs** for the contents of BAA, BAP, BBF, CHR, and the SUM parameters in the spiked olive oil test material.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the questionable and non-satisfactory results.

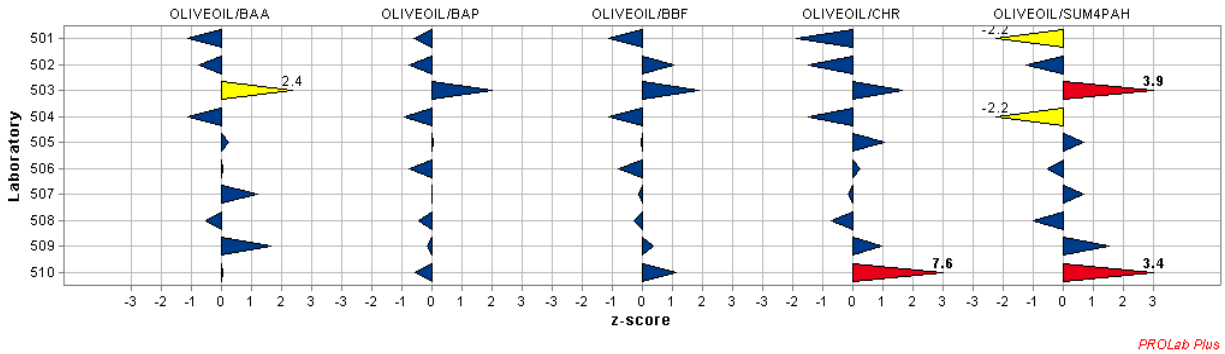


**Table 5: Compilation of z-scores calculated from the "final results" reported by the NRLs and OCLs for test material OIL: z-scores outside the satisfactory range (|z| > 2) are highlighted in red.**

| | BAA | | BAP | | BBF | | CHR | | SUM | |
|---|---|---|---|---|---|---|---|---|---|---|
| Assigned value, µg/kg | 3.91 | | 2.97 | | 1.71 | | 2.46 | | 11.06 | |
| σp, µg/kg | 0.80 | | 0.61 | | 0.37 | | 0.51 | | 1.19 | |
| | Result | z-score | Result | z-score | Result | z-score | Result | z-score | Result | z-score |
| **Lab code** | µg/kg | | µg/kg | | µg/kg | | µg/kg | | µg/kg | |
| | **National Reference Laboratories (NRLs)** | | | | | | | | | |
| 101 | 3.93 | 0.0 | 2.9 | -0.1 | 1.71 | 0.0 | 2.34 | -0.2 | 10.88 | -0.2 |
| 102 | 3.92 | 0.0 | 3.09 | 0.2 | 1.87 | 0.4 | 2.46 | 0.0 | 11.34 | 0.2 |
| 103 | 4.53 | 0.8 | 3.29 | 0.5 | 2.26 | 1.5 | 2.96 | 1.0 | 13.04 | 1.7 |
| 104 | 4.1 | 0.2 | 2.9 | -0.1 | 1.7 | 0.0 | 2.3 | -0.3 | 8.3 | -2.3 |
| 105 | 2.94 | -1.2 | 3.01 | 0.1 | 1.5 | -0.6 | 1.66 | -1.6 | 9.12 | -1.6 |
| 106 | 3.99 | 0.1 | 2.87 | -0.2 | 1.59 | -0.3 | 1.83 | -1.2 | 10.32 | -0.6 |
| 107 | 3.7 | -0.3 | 3.6 | 1.0 | 1.3 | -1.1 | 2 | -0.9 | 11 | -0.1 |
| 108 | 4.3 | 0.5 | 3.01 | 0.1 | 1.77 | 0.2 | 2.68 | 0.4 | 11.8 | 0.6 |
| 109 | 1.82 | -2.6 | 1.66 | -2.1 | 1 | -1.9 | 1.5 | -1.9 | 5.98 | -4.3 |
| 110 | 4.1 | 0.2 | 2.52 | -0.7 | 1.46 | -0.7 | 1.87 | -1.2 | 9.95 | -0.9 |
| 111 | 3.57 | -0.4 | 3.01 | 0.1 | 1.92 | 0.6 | 4.66 | 4.3 | 13.15 | 1.8 |
| 112 | 2.95 | -1.2 | 3.43 | 0.8 | 2.72 | 2.7 | 2.47 | 0.0 | 11.57 | 0.4 |
| 113 | 4.1 | 0.2 | 3.3 | 0.5 | 1.8 | 0.2 | 2.6 | 0.3 | 11.8 | 0.6 |
| 114 | 4.7 | 1.0 | 3.65 | 1.1 | 2.34 | 1.7 | 3.02 | 1.1 | 13.72 | 2.2 |
| 115 | 3.52 | -0.5 | 3.01 | 0.1 | 1.89 | 0.5 | 2.42 | -0.1 | 10.8 | -0.2 |
| 116 | 3.66 | -0.3 | 3.07 | 0.2 | 1.85 | 0.4 | 2.04 | -0.8 | 10.62 | -0.4 |
| 117 | 3.46 | -0.6 | 2.66 | -0.5 | 1.48 | -0.6 | 2.25 | -0.4 | 9.86 | -1.0 |
| 118 | 3.98 | 0.1 | 2.89 | -0.1 | 1.78 | 0.2 | 2.48 | 0.0 | 11.13 | 0.1 |
| 119 | 3.97 | 0.1 | 2.74 | -0.4 | 1.81 | 0.3 | 2.57 | 0.2 | 11.09 | 0.0 |
| 120 | 4.05 | 0.2 | 2.69 | -0.5 | 1.85 | 0.4 | 3.17 | 1.4 | 11.75 | 0.6 |
| 121 | 3.85 | -0.1 | 2.56 | -0.7 | 1.81 | 0.3 | 2.67 | 0.4 | 10.9 | -0.1 |
| 122 | 3.86 | -0.1 | 2.83 | -0.2 | 1.63 | -0.2 | 2.14 | -0.6 | 10.5 | -0.5 |
| 123 | 3.59 | -0.4 | 2.87 | -0.2 | 1.52 | -0.5 | 2.31 | -0.3 | 10.29 | -0.6 |
| 124 | 4.08 | 0.2 | 3.21 | 0.4 | 1.84 | 0.4 | 2.93 | 0.9 | 12.06 | 0.8 |
| 125 | 4.26 | 0.4 | 4.034 | 1.7 | 2.375 | 1.8 | 3.457 | 2.0 | 14.127 | 2.6 |
| 126 | 3.6 | -0.4 | 3.2 | 0.4 | 1.2 | -1.4 | 2.7 | 0.5 | 10.7 | -0.3 |
| | **Official control laboratories (OCLs)** | | | | | | | | | |
| 501 | 3 | -1.1 | 2.6 | -0.6 | 1.3 | -1.1 | 1.5 | -1.9 | 8.4 | -2.2 |
| 502 | 3.3 | -0.8 | 2.5 | -0.8 | 2.1 | 1.1 | 1.7 | -1.5 | 9.6 | -1.2 |
| 503 | 5.8 | 2.4 | 4.2 | 2.0 | 2.4 | 1.9 | 3.3 | 1.6 | 15.7 | 3.9 |
| 504 | 3 | -1.1 | 2.4 | -0.9 | 1.3 | -1.1 | 1.7 | -1.5 | 8.4 | -2.2 |
| 505 | 4.1 | 0.2 | 3 | 0.0 | 1.7 | 0.0 | 3 | 1.1 | 11.9 | 0.7 |
| 506 | 3.93 | 0.0 | 2.5 | -0.8 | 1.42 | -0.8 | 2.59 | 0.3 | 10.44 | -0.5 |
| 507 | 4.86 | 1.2 | 2.97 | 0.0 | 1.66 | -0.1 | 2.38 | -0.2 | 11.87 | 0.7 |
| 508 | 3.5 | -0.5 | 2.7 | -0.4 | 1.6 | -0.3 | 2.1 | -0.7 | 9.9 | -1.0 |
| 509 | 5.227 | 1.6 | 2.878 | -0.2 | 1.842 | 0.4 | 2.944 | 0.9 | 12.891 | 1.5 |
| 510 | 3.95 | 0.1 | 2.63 | -0.6 | 2.12 | 1.1 | 6.36 | 7.6 | 15.07 | 3.4 |

**Table 6: Compilation of zeta-scores calculated from the "results for proficiency assessment" reported by the NRLs and OCLs for test item OIL, the combined reported standard measurement uncertainty, and the uncertainty of the analyte content of the test material:**

zeta-scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function $U_f$ (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter).

| | BAA | | | BAP | | | BBF | | | CHR | | | SUM | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Assigned value +/- U, µg/kg | 3.91 | ± | 0.14 | 2.97 | ± | 0.34 | 1.71 | ± | 0.27 | 2.46 | ± | 0.22 | 11.06 | ± | 0.5 |
| $\sigma_r$, µg/kg | 0.8 | | | 0.61 | | | 0.37 | | | 0.51 | | | 1.19 | | |
| | Result | U | zeta-score | Result | U | zeta-score | Result | U | zeta-score | Result | U | zeta-score | Result | U | zeta-score |
| Lab code | µg/kg | µg/kg | | µg/kg | µg/kg | | µg/kg | µg/kg | | µg/kg | µg/kg | | µg/kg | µg/kg | |
| | National Reference Laboratories (NRLs) | | | | | | | | | | | | | | |
| 101 | 3.93 | 0.62 | 0.1 | 2.9 | 0.52 | -0.2 | 1.71 | 0.31 | 0.0 | 2.34 | 0.38 | -0.4 | 10.88 | 0.95 | -0.3 |
| 102 | 3.92 | 0.59 | 0.0 | 3.09 | 0.31 | 0.3 | 1.87 | 0.28 | 0.5 | 2.46 | 0.31 | 0.0 | 11.34 | 0.79 | 0.4 |
| 103 | 4.53 | 0.39 | 2.6 | 3.29 | 0.25 | 0.9 | 2.26 | 0.17 | 1.9 | 2.96 | 0.22 | 2.0 | 13.04 | 0.54 | 3.5 |
| 104 | 4.1 | 1.7 | 0.2 | 2.9 | 1.2 | -0.1 | 1.7 | 0.7 | 0.0 | 2.3 | 1 | -0.3 | 8.3 | 4.6 | -1.2 |
| 105 | 2.94 | 0.44 | -3.7 | 3.01 | 0.39 | 0.1 | 1.5 | 0.24 | -0.7 | 1.66 | 0.23 | -3.2 | 9.12 | 0.68 | -3.2 |
| 106 | 3.99 | 0.61 | 0.2 | 2.87 | 0.47 | -0.2 | 1.59 | 0.27 | -0.4 | 1.83 | 0.33 | -2.3 | 10.32 | 2.01 | -0.7 |
| 107 | 3.7 | 1.1 | -0.4 | 3.6 | 1.1 | 1.0 | 1.3 | 0.4 | -1.2 | 2 | 0.6 | -1.2 | 11 | 1.7 | -0.1 |
| 108 | 4.3 | 0.64 | 1.1 | 3.01 | 0.3 | 0.1 | 1.77 | 0.35 | 0.2 | 2.68 | 0.54 | 0.6 | 11.8 | 1.18 | 1.0 |
| 109 | 1.82 | 0.23 | -11.5 | 1.66 | 0.25 | -3.6 | 1 | 0.14 | -2.5 | 1.5 | 0.29 | -3.6 | 5.98 | 0.84 | -7.8 |
| 110 | 4.1 | 0.98 | 0.4 | 2.52 | 0.6 | -1.0 | 1.46 | 0.26 | -0.8 | 1.87 | 0.34 | -2.1 | 9.95 | 1.23 | -1.4 |
| 111 | 3.57 | 0.71 | -0.9 | 3.01 | 0.6 | 0.1 | 1.92 | 0.38 | 0.6 | 4.66 | 0.94 | 4.2 | 13.15 | 1.38 | 2.5 |
| 112 | 2.95 | 0.3 | -4.7 | 3.43 | 0.3 | 1.2 | 2.72 | 0.3 | 3.3 | 2.47 | 0.3 | 0.0 | 11.57 | 1.1 | 0.7 |
| 113 | 4.1 | 1 | 0.4 | 3.3 | 0.6 | 0.7 | 1.8 | 0.6 | 0.2 | 2.6 | 0.5 | 0.4 | 11.8 | 1.4 | 0.9 |
| 114 | 4.7 | 0.31 | 3.8 | 3.65 | 0.11 | 2.0 | 2.34 | 0.7 | 1.4 | 3.02 | 0.32 | 2.1 | 13.72 | 0.8 | 4.2 |
| 115 | 3.52 | 0.88 | -0.8 | 3.01 | 0.75 | 0.1 | 1.89 | 0.47 | 0.5 | 2.42 | 0.6 | -0.1 | 10.8 | 2.71 | -0.2 |
| 116 | 3.66 | 0.74 | -0.6 | 3.07 | 0.62 | 0.2 | 1.85 | 0.4 | 0.4 | 2.04 | 0.41 | -1.4 | 10.62 | 1.12 | -0.6 |
| 117 | 3.46 | 0.74 | -1.1 | 2.66 | 0.5 | -0.7 | 1.48 | 0.31 | -0.7 | 2.25 | 0.54 | -0.6 | 9.86 | 1.73 | -1.2 |
| 118 | 3.98 | 0.89 | 0.2 | 2.89 | 0.54 | -0.2 | 1.78 | 0.29 | 0.2 | 2.48 | 0.68 | 0.0 | 11.13 | 2.24 | 0.1 |
| 119 | 3.97 | 0.79 | 0.1 | 2.74 | 0.34 | -0.6 | 1.81 | 0.36 | 0.3 | 2.57 | 0.51 | 0.3 | 11.09 | 2.22 | 0.0 |
| 120 | 4.05 | 0.68 | 0.4 | 2.69 | 0.4 | -0.7 | 1.85 | 0.26 | 0.5 | 3.17 | 0.51 | 2.1 | 11.75 | 2 | 0.6 |
| 121 | 3.85 | 0.4 | -0.2 | 2.56 | 0.3 | -1.1 | 1.81 | 0.2 | 0.3 | 2.67 | 0.3 | 0.8 | 10.9 | 1 | -0.2 |
| 122 | 3.86 | 0.35 | -0.2 | 2.83 | 0.33 | -0.4 | 1.63 | 0.36 | -0.2 | 2.14 | 0.37 | -1.1 | 10.5 | 0.71 | -0.9 |
| 123 | 3.59 | 0.93 | -0.7 | 2.87 | 0.97 | -0.2 | 1.52 | 0.46 | -0.5 | 2.31 | 0.51 | -0.4 | 10.29 | 1.51 | -0.9 |
| 124 | 4.08 | 0.77 | 0.4 | 3.21 | 0.87 | 0.4 | 1.84 | 0.51 | 0.4 | 2.93 | 1.12 | 0.8 | 12.06 | 1.69 | 1.0 |
| 125 | 4.26 | 1.431 | 0.5 | 4.034 | 1.121 | 1.6 | 2.375 | 0.613 | 1.6 | 3.457 | 0.957 | 1.9 | 14.127 | 4.123 | 1.4 |
| 126 | 3.6 | 0.73 | -0.8 | 3.2 | 0.64 | 0.5 | 1.2 | 0.24 | -1.7 | 2.7 | 0.54 | 0.7 | 10.7 | 1.14 | -0.5 |
| | Official Control Laboratories (OCLs) | | | | | | | | | | | | | | |
| 501 | 3 | 0.1 | -6.1 | 2.6 | 0.1 | -1.1 | 1.3 | 0.4 | -1.2 | 1.5 | 0.1 | -4.3 | 8.4 | 0.5 | -4.8 |
| 502 | 3.3 | n.r. | | 2.5 | n.r. | | 2.1 | n.r. | | 1.7 | n.r. | | 9.6 | n.r. | |
| 503 | 5.8 | n.r. | | 4.2 | n.r. | | 2.4 | n.r. | | 3.3 | n.r. | | 15.7 | n.r. | |
| 504 | 3 | 1.2 | -1.5 | 2.4 | 0.6 | -1.3 | 1.3 | 0.4 | -1.2 | 1.7 | 0.6 | -2.0 | 8.4 | 2.7 | -1.8 |
| 505 | 4.1 | 0.9 | 0.4 | 3 | 0.7 | 0.1 | 1.7 | 0.4 | 0.0 | 3 | 0.6 | 1.5 | 11.9 | 1.3 | 1.0 |
| 506 | 3.93 | 1.3 | 0.0 | 2.5 | 0.55 | -1.1 | 1.42 | 0.4 | -0.9 | 2.59 | 1.03 | 0.2 | 10.44 | 1.71 | -0.6 |
| 507 | 4.86 | 0.49 | 3.4 | 2.97 | 0.59 | 0.0 | 1.66 | 0.17 | -0.2 | 2.38 | 0.48 | -0.2 | 11.87 | 2.37 | 0.6 |
| 508 | 3.5 | 0.7 | -1.1 | 2.7 | 0.5 | -0.6 | 1.6 | 0.3 | -0.4 | 2.1 | 0.4 | -1.2 | 9.9 | 2 | -1.0 |
| 509 | 5.227 | 1.0454 | 2.4 | 2.878 | 5.756 | 0.0 | 1.842 | 0.3684 | 0.4 | 2.944 | 0.5888 | 1.3 | 12.891 | 2.578 | 1.3 |
| 510 | 3.95 | 1.18 | 0.1 | 2.63 | 0.79 | -0.7 | 2.12 | 0.64 | 1.0 | 6.36 | 1.9 | 4.0 | 15.07 | 5 | 1.6 |

n.r.: not reported

The figures in ANNEX 9 are an aid to allow laboratories to compare the performance of their method to those of other participants with respect to bias (closeness to the assigned value, plotted on the x-axis) and precision (the standard deviation for repeatability, plotted on the y-axis). A vertical solid bold line depicts the assigned value; laboratories are represented by blue dots (mean value of the replicates and the associated standard deviation of the replicates). The light blue area indicates the satisfactory performance area, which is defined by the assigned value $\pm 2\sigma_P$ along the x-axis and by the average repeatability standard deviation of the results reported by the participants along the y-axis. The latter was obtained by analysis-of-variance of the data set received for each analyte. Participants whose data are outside the satisfactory performance area should perform root cause analysis. They are required to report back to the EURL PAH the identified reason for their deviations.

## 9.4 Evaluation of the reported performance parameters for the methods applied

The characteristics of the methods applied by participants and the results reported are listed in ANNEX 7.

Compliance with legislation was evaluated on basis of requirements set in Regulation (EC) No 333/2007 as amended by Regulation (EU) No 836/2011 [7]. Non-compliant values for LOD, LOQ, and recovery are indicated by bold red font.

The values for recovery complied with the limits specified in Commission Regulation (EU) No 836/2011. However, it cannot be evaluated whether recovery was understood as yield, as requested and not as apparent recovery, which might be indicated by recovery values close to 100 %.

One NRL reported non-compliant LOD/LOQ and three participants (2NRLs and 1 OCL) did not report any LOD/LOQ values. Additionally 5 OCLs did not reported information on the working range of their method. About 50% of laboratories reported lower limits of the working range of their analysis method lower than the corresponding LOQ. These values are marked with yellow. Three of those participant reported lower limit of the working range even lower than LOD. Those values are marked in red bold font additionally.

The observed discrepancy between the LOQ and the lower limit for the working range should be taken into consideration by the respective laboratories. Actions should be taken for more realistic estimation of the LOD/LOQ or for better fitting the lower limit of the working range with the estimated LOQ limits. That shortcoming will be addressed on the next workshop.

The evaluation of the compliance of reported measurement uncertainties with provisions given in legislation was discussed before.

## 9.5 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled in by the participants (ANNEX 7). Data is presented as reported.

Regarding the experience of the laboratories with this kind of analysis 28 laboratories reported experience of more than four years, but 7 laboratories do not analysed more than 10 samples per year, indicating that they do not perform the analysis on a routine basis. The distribution in terms of years of experience and number of analysis per year between NRLs and OCLs is shown in Figure 3 and 4.

All participants are accredited except 2 OCL laboratories.

**Figure 3**. Experience of the participants in years in the analysis of PAH in edible oil

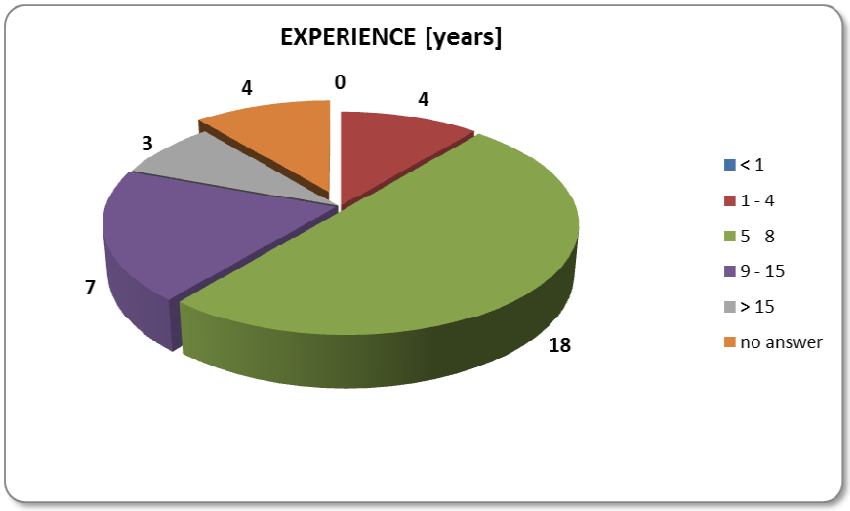



**Figure 4**. Experience of the participants in the analysis of PAH in edible oil expressed as number of analyses per years

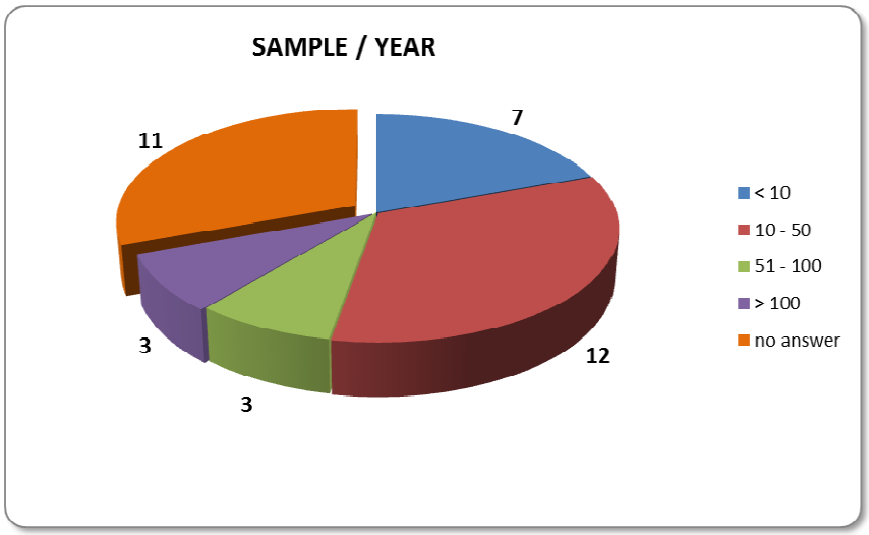
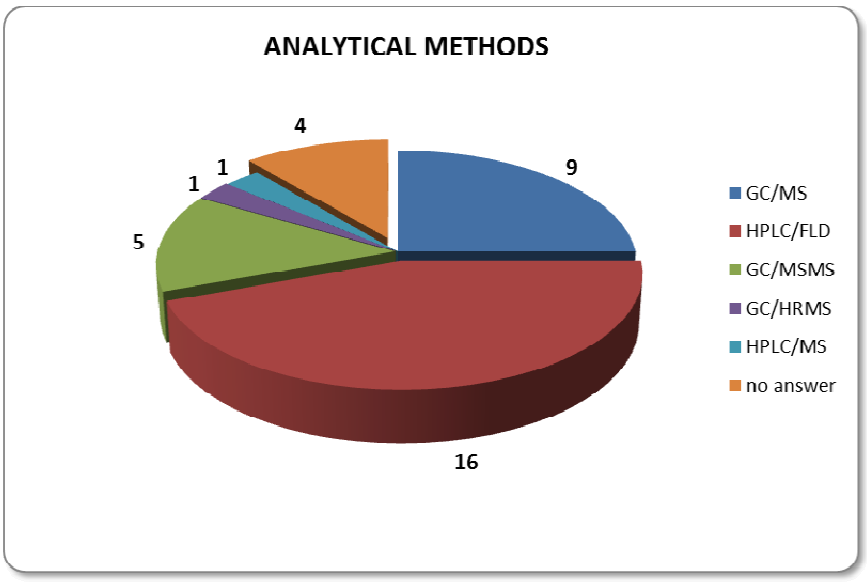



**Figure 5**. Application of different instrumental methods for determination of PAH in edible oil.



More than half of the participants (NRLs and OCLs) used HPLC/FLD (1 lab LC/MS) techniques for PAHs determination (Figure 5). The analysis of all data revealed that laboratory performance was not linked to any analytical technique or sample preparation method used.

Finally, ANNEX 7 summarises the comments of the participants regarding the organised interlaboratory comparison.

For the first time EURL asked participants (NRLs and official control laboratories) to assess the compliance of the sample according to the legislative limits. Based on the assigned values, the sample is non-compliant concerning both BaP and sum of the four PAHs regarding the MLs specified for the food category 6.1.1 "Oils and fats, intended for direct human consumption or use as an ingredient in food" specified in Commission Regulation (EC) No 835/2011. The maximum levels (ML) for BAP and for the sum of the four PAHs are 2.0 µg/kg and 10.0 µg/kg respectively.

Figure 6 presents the distribution of the reported results and their uncertainties for BaP and the SUM of the 4 PAHs in relation to the maximum limits defined in the legislation.

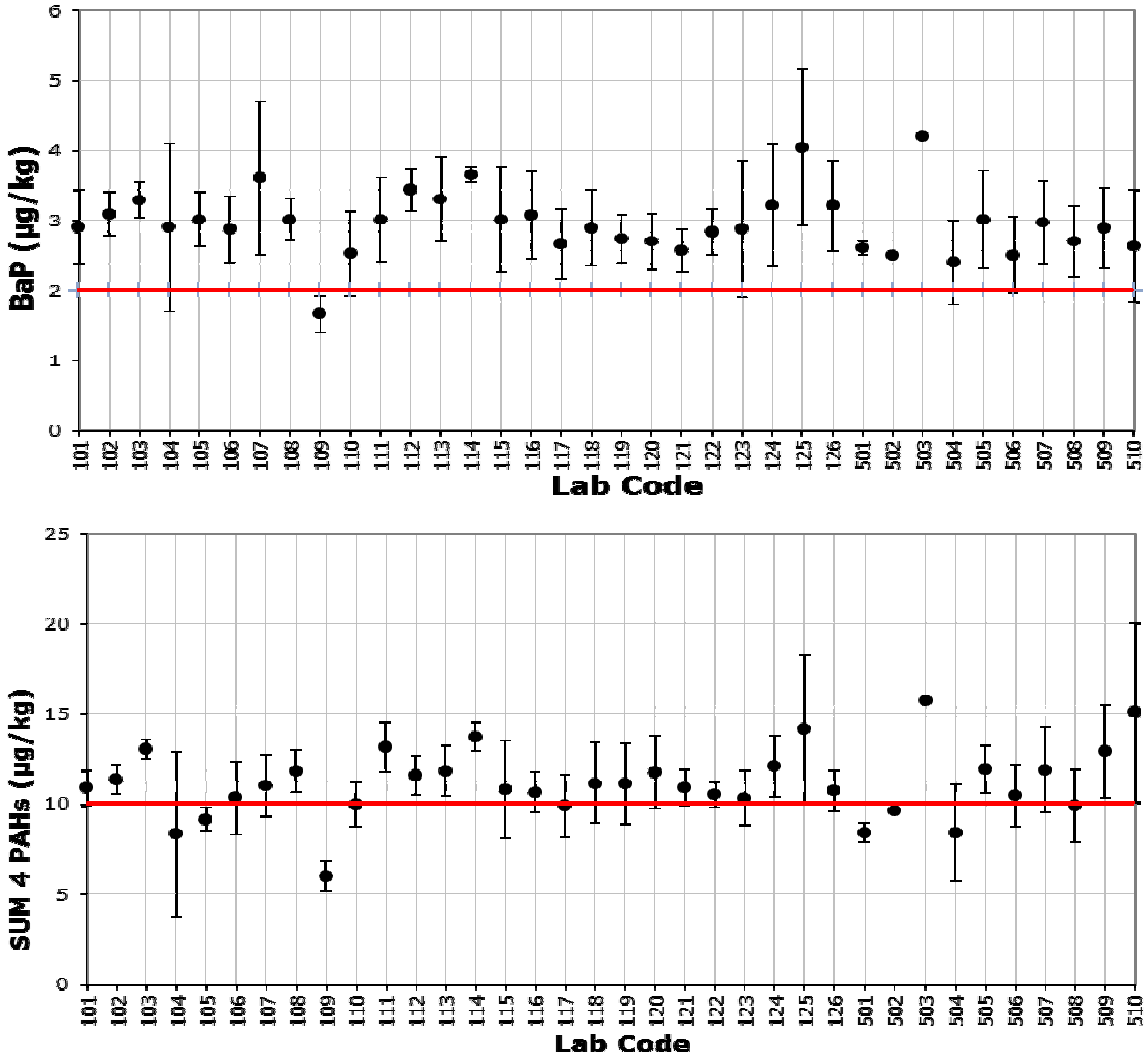
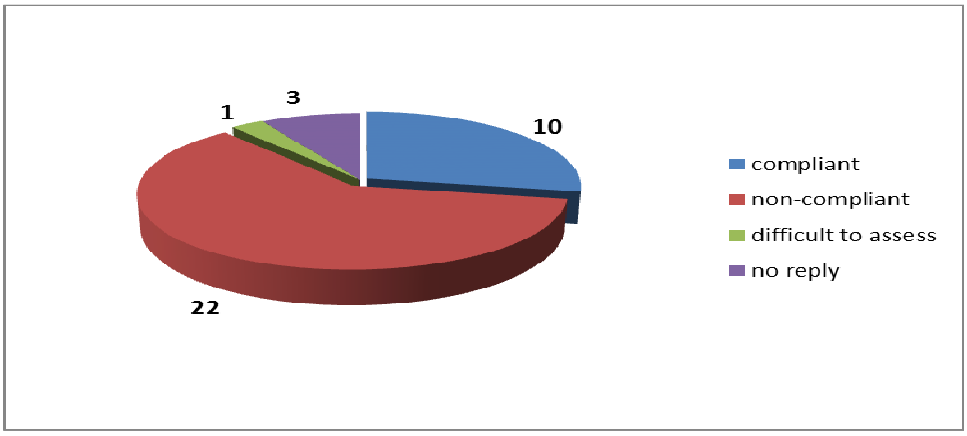



**Figure 6**. Distribution of the results reported by the participants and the associated expanded measurement uncertainties for BaP and the SUM PAHs in relation to the MLs.

*Red line represents the maximum limits (MLs) defined in the Commission Regulation (EC) No 835/2011, 2.0 µg/kg for BAP and 10.0 µg/kg for the sum of the four PAHs respectively. The sample has to be declared as non-compliant if the concentration value provided by the measurement result minus the expanded measurement uncertainty is larger than the ML.*

An overview of the participant responses concerning the sample's compliance with the legislative limits results is presented on Figure 7. Ten out of 36 control laboratories (28%) assessed the sample as compliant in the questionnaire. Five out of that 10 participants however wrongly categorised it as compliant as they reported BaP reduced by the associated MU was above the ML, and for lab 124 also the (SUM PAH - U) > ML. Further investigation should be carried out concerning the algorithm according to which the control laboratories asses the compliance of a sample with the legislation. They should follow the recommendation of the EURACHEM guide "Use of uncertainty information in compliance assessment" [14].

**Figure 7.** Participants' responses concerning compliance of the sample (olive oil) with the MLs defined in the Commission Regulation (EC) No 835/2011.




## 10. Follow-up actions for underperforming laboratories

All NRL laboratories that got "questionable" or "unsatisfactory" performance ratings are urged to perform root cause analysis, and to implement corrective actions.

The EURL will set up follow-up measures in due time for all NRLs that received for at least one of the four PAHs (BAA, BAP, BBF, and CHR) |z-scores | > 3 as required by Regulation (EC) 882/2004, and by the Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with European Union reference laboratories (EURLs) activities. These laboratories shall perform as an immediate action a root-cause-analysis, and shall report to the EURL PAH in writing, the identified cause for their underperformance and the corrective actions they are going to take.

## 11. Conclusions

Thirty six participants reported analysis results. The performance of most participants was satisfactory. In total 94 % and 88 % of the results reported by NRLs and OCLs respectively obtained a satisfactory z-score. zeta-Scores were calculated besides z-scores. They indicate the agreement of the reported result with the assigned value with respect to the stated measurement uncertainty. The outcome of this rating was worse than for the z-scores, which reveals that the measurement uncertainty estimates were in some cases not realistic. For the first time participants were asked to assess the compliance of the sample according to the legislative limits. Five out of that 10 participants however wrongly categorised it as compliant.

## 12. Acknowledgements

The organizers would like to thank Beatriz de la Calle and Franz Ulberth (from IRMM, Geel, Belgium) for their accurate revision of this report and all NRLs and OCLs for their cooperation.

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# 14. ANNEXES

ANNEX 1 – Announcement of the PT on the IRMM webpage

ANNEX 2 – Announcement via e-mail and invitation

ANNEX 3 – Announcement of material dispatch

ANNEX 4 – Documents sent to participants

ANNEX 5 – Technical specifications of the calibration solutions

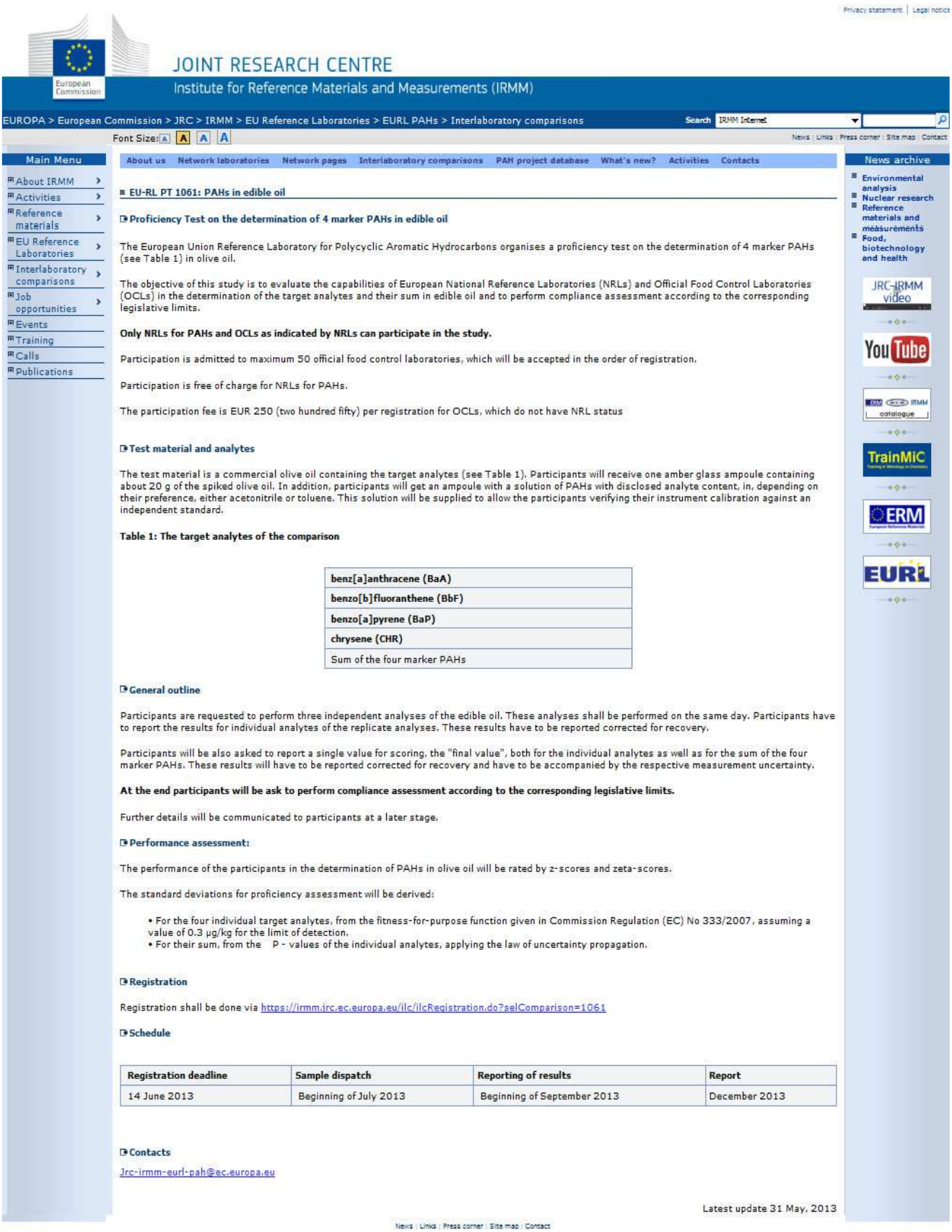
ANNEX 6 – Homogeneity of the test material

ANNEX 7 – Questionnaire and method performance data

ANNEX 8 – Data reported by participants

ANNEX 9 - Laboratory means and repeatability standard deviation

# ANNEX 1: Announcement of the PT on the IRMM webpage



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European Commission

JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (IRMM)

EUROPA > European Commission > JRC > IRMM > EU Reference Laboratories > EURL PAHs > Interlaboratory comparisons

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## EU-RL PT 1061: PAHs in edible oil

### Proficiency Test on the determination of 4 marker PAHs in edible oil

The European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons organises a proficiency test on the determination of 4 marker PAHs (see Table 1) in olive oil.

The objective of this study is to evaluate the capabilities of European National Reference Laboratories (NRLs) and Official Food Control Laboratories (OCLs) in the determination of the target analytes and their sum in edible oil and to perform compliance assessment according to the corresponding legislative limits.

**Only NRLs for PAHs and OCLs as indicated by NRLs can participate in the study.**

Participation is admitted to maximum 50 official food control laboratories, which will be accepted in the order of registration.

Participation is free of charge for NRLs for PAHs.

The participation fee is EUR 250 (two hundred fifty) per registration for OCLs, which do not have NRL status

### Test material and analytes

The test material is a commercial olive oil containing the target analytes (see Table 1). Participants will receive one amber glass ampoule containing about 20 g of the spiked olive oil. In addition, participants will get an ampoule with a solution of PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene. This solution will be supplied to allow the participants verifying their instrument calibration against an independent standard.

**Table 1: The target analytes of the comparison**

| |
|---|
| **benz[a]anthracene (BaA)** |
| **benzo[b]fluoranthene (BbF)** |
| **benzo[a]pyrene (BaP)** |
| **chrysene (CHR)** |
| Sum of the four marker PAHs |

### General outline

Participants are requested to perform three independent analyses of the edible oil. These analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. These results have to be reported corrected for recovery.

Participants will be also asked to report a single value for scoring, the "final value", both for the individual analytes as well as for the sum of the four marker PAHs. These results will have to be reported corrected for recovery and have to be accompanied by the respective measurement uncertainty.

**At the end participants will be ask to perform compliance assessment according to the corresponding legislative limits.**

Further details will be communicated to participants at a later stage.

### Performance assessment:

The performance of the participants in the determination of PAHs in olive oil will be rated by z-scores and zeta-scores.

The standard deviations for proficiency assessment will be derived:

- For the four individual target analytes, from the fitness-for-purpose function given in Commission Regulation (EC) No 333/2007, assuming a value of 0.3 µg/kg for the limit of detection.
- For their sum, from the P - values of the individual analytes, applying the law of uncertainty propagation.

### Registration

Registration shall be done via https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=1061

### Schedule

| Registration deadline | Sample dispatch | Reporting of results | Report |
|---|---|---|---|
| 14 June 2013 | Beginning of July 2013 | Beginning of September 2013 | December 2013 |

### Contacts

Jrc-irmm-eurl-pah@ec.europa.eu

Latest update 31 May, 2013

News | Links | Press corner | Site map | Contact

## ANNEX 2: Announcement of the PT via invitation

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 28/05/2013
Ref. Ares(2013)1499322 - 29/05/2013

**Interlaboratory comparison of the EU-RL for Polycyclic Aromatic Hydrocarbons (PAHs) in olive oil**

Dear Madame/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EU-RL PAH on the determination of the 4 marker PAHs in olive oil will be **open from 30th May to 14th June 2013**.

Participation is mandatory and free of charge for National Reference Laboratories (NRLs) for PAHs. Confidentiality of participants and respective results is granted.

In support to the NRLs, to facilitate fulfilling their tasks as included in Regulation (EC) No 882/2004, EU Official Food Control Laboratories (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 250 Euro per participation.**

The target analytes are listed in the following Table.

| |
|---|
| benz[a]anthracene (BaA) |
| benzo[b]fluoranthene (BbF) |
| benzo[a]pyrene (BaP) |
| chrysene (CHR) |
| SUM of the 4 marker PAHs |

Results have to be reported corrected for recovery and accompanied by the respective measurement uncertainty for both the individual PAHs and the sum of the four marker PAHs. **Additionally participants will be asked to perform compliance assessment according to the corresponding legislative limits.**

Retieseweg 111, B-2440 Geel – Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 820. Fax: (32-14) 571 783
E-mail: jrc-irmm-crl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Each participant will be provided with one amber glass ampoule containing ~ 20 g of olive oil. **In case you need more than 1 ampoule, please express your justified request before the sample dispatch.**

Participants will also receive a standard solution in either acetonitrile or toluene with disclosed content; which might be used for verification of instrument calibration.

This inter-laboratory comparison is organised under accreditation to ISO 17043.

**Detailed information will be soon available the EU-RL website:**
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

**Timing:**

- **Deadline for registration: 14 June 2013**
- Dispatch of samples: **beginning of July.** A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser.
- Deadline for reporting of results: **beginning of September.** You will receive the link for entering the results upon reception of the PT samples

**Registration procedure:**
**Participants** shall register via this link:
https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=1061

In order to register, laboratories must:

1. **Enter** the details on line:
2. **Print** the completed form (approved and confirmed version) when the system asks to do so, sign it and stamp it with your company stamp
3. **Send** it to the EU-RL PAHs members indicated below, either via FAX or via e-mail

| **PT coordinator** | **Second contact** |
|---|---|
| Stefanka Bratinova | Zuzana Zelinkova |
| Fax: 0032-14-571783<br>e-mail: jrc-irmm-eurl-pah@ec.europa.eu | |

Participants will be requested to indicate the preferred solvent type of the standard solutions (either toluene or acetonitrile) prior to dispatch of samples via a separate email.

Retieseweg 111, B-2440 Geel – Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 820. Fax: (32-14) 571 783
E-mail: jrc-irmm-crl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

**Distribution of information:**

The NRLs are kindly requested to distribute as soon as possible this information to the OCLs under their responsibility, and to assist the EU-RL in identifying laboratories that are eligible to participate in the study.

**Access of NRLs to performance data of official food control laboratories:**

**Two options:**

1) *NRL enrols OCLs and covers participation fee.*

   NRL submits to EU-RL list of participants including name and address of laboratory, and details of the contact person (name, address - no post box! -, email and telephone number). The coverage of the participation fees has to be confirmed and details for invoicing (e.g. order number) have to be provided. It shall be made clear, that the full participation fee is payable upon dispatch of the test samples. In return, the performance data of the respective official food control laboratories will be disclosed to the NRL.

2) The *OCL (identified as such by the respective NRL) enrols itself* in the inter-laboratory comparison *and covers the participation fee.*

   The NRL will get access to performance data of the OCL only upon providing to the EU-RL for PAHs a letter of consent.

In case you may wish clarification of open questions, please do not hesitate to contact the EU-RL team via:

JRC-IRMM-EURL-PAH@ec.europa.eu

With kind regards,

Stefanka Bratinova

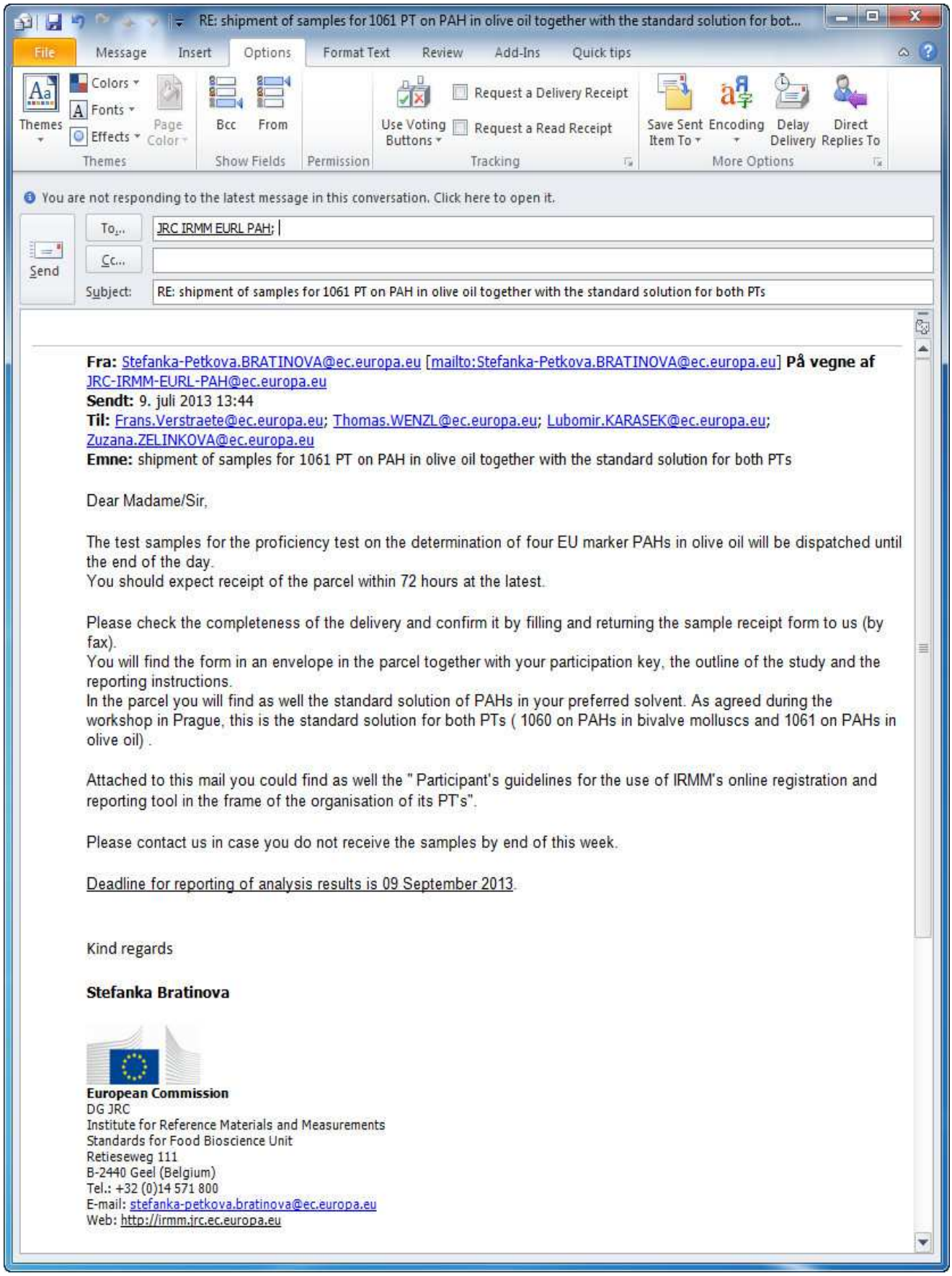
Cc: Thomas Wenzl, Beatriz de la Calle, Franz Ulberth

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783

E-mail: jrc-irmm-eurl-pah@ec.europa.eu

Web site: http://irmm.jrc.ec.europa.eu/

## ANNEX 3: Announcement of material dispatch



RE: shipment of samples for 1061 PT on PAH in olive oil together with the standard solution for bot...

File | Message | Insert | Options | Format Text | Review | Add-Ins | Quick tips

Themes | Colors | Fonts | Effects | Page Color | Bcc | From | Use Voting Buttons | Request a Delivery Receipt | Request a Read Receipt | Save Sent Item To | Encoding | Delay Delivery | Direct Replies To

Themes | Show Fields | Permission | Tracking | More Options

You are not responding to the latest message in this conversation. Click here to open it.

Send | To... JRC IRMM EURL PAH; | Cc... | Subject: RE: shipment of samples for 1061 PT on PAH in olive oil together with the standard solution for both PTs

**Fra:** Stefanka-Petkova.BRATINOVA@ec.europa.eu [mailto:Stefanka-Petkova.BRATINOVA@ec.europa.eu] **På vegne af** JRC-IRMM-EURL-PAH@ec.europa.eu
**Sendt:** 9. juli 2013 13:44
**Til:** Frans.Verstraete@ec.europa.eu; Thomas.WENZL@ec.europa.eu; Lubomir.KARASEK@ec.europa.eu; Zuzana.ZELINKOVA@ec.europa.eu
**Emne:** shipment of samples for 1061 PT on PAH in olive oil together with the standard solution for both PTs

Dear Madame/Sir,

The test samples for the proficiency test on the determination of four EU marker PAHs in olive oil will be dispatched until the end of the day.
You should expect receipt of the parcel within 72 hours at the latest.

Please check the completeness of the delivery and confirm it by filling and returning the sample receipt form to us (by fax).
You will find the form in an envelope in the parcel together with your participation key, the outline of the study and the reporting instructions.
In the parcel you will find as well the standard solution of PAHs in your preferred solvent. As agreed during the workshop in Prague, this is the standard solution for both PTs ( 1060 on PAHs in bivalve molluscs and 1061 on PAHs in olive oil) .

Attached to this mail you could find as well the " Participant's guidelines for the use of IRMM's online registration and reporting tool in the frame of the organisation of its PT's".

Please contact us in case you do not receive the samples by end of this week.

Deadline for reporting of analysis results is 09 September 2013.

Kind regards

**Stefanka Bratinova**

**European Commission**
DG JRC
Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit
Retieseweg 111
B-2440 Geel (Belgium)
Tel.: +32 (0)14 571 800
E-mail: stefanka-petkova.bratinova@ec.europa.eu
Web: http://irmm.jrc.ec.europa.eu

## ANNEX 4: Documents sent to participants - OUTLINE

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 25/06/2013

**ILC-1061**

**Thirteenth inter-laboratory comparison study organised by the EU-RL PAHs**

***Analysis of the four marker PAHs in olive oil***

### General description

The test material is olive oil. Target analytes are the four marker PAHs (listed in Table 1). Additionally laboratories have to report their sum.

The EU-RL PAHs will check for the four target analytes the compliance of the performed analyses with provisions given in Regulation (EU) No 836/2011.

Participating laboratories will be scored for each of the four PAHs, plus for their sum.

**Table 1: The target analytes of the comparison (four marker PAHs)**

| |
|---|
| benz[*a*]anthracene (BaA) |
| benzo[*b*]fluoranthene (BbF) |
| benzo[*a*]pyrene (BaP) |
| chrysene (CHR) |
| SUM of the 4 marker PAHs |

### The content of the parcel

Each participant will be provided with a set of samples that comprises:

- One ampoule, labelled "Interlaboratory comparison 1061 4 EU-PAHs in edible oil/XXX", containing about 20 g of spiked olive oil. The concentration of the individual analytes is in the range from about 0 to 20 µg/kg. This sample **is the test sample of the PT.**
- One ampoule, labelled as "ACN-10/2012-K/XXX" or as "TOL-10/2012-K/XXX" depending on the solvent you chose, acetonitrile or toluene respectively, containing about 1 ml of a solution of the *four marker PAHs in solvent (acetonitrile or toluene).* The concentration of the individual analytes is reported in the respective specification sheet and is therefore **known to participants.** Please bear in mind that these solutions *do not contain any internal standards.*

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Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783
E-mail: jrc-irmm-crl-pah@ec.europa.eu

**Olive oil samples are to be stored at room temperature and solutions at 4°C in the dark**

Participants will also receive:

- the a sample receipt form (to be filled in and sent back to the EU-RL as soon as possible)
- the outline of the study (a printout of this document)
- the participation/password key (to be used only for entering the results for this PT) and the laboratory code which will be used in the Final Report.
- specification sheets for the solutions of known content
- material safety data sheets for some of the analytes and for the solvents

### Outline of the study

1. The laboratories are requested to perform **three (3) replicate analyses on the contaminated olive oil material.** The sample shall be analysed immediately after opening of the ampoule, and the three replicates should be analysed under repeatability condition. A **"final value", which is the value applied for scoring,** is also required for each analyte beside the results obtained from replicate analysis. In addition, participants are asked to report a value for the sum of the four target PAHs.
2. The **known solution of PAHs in solvent** may be used by participants as an external reference to check their instrument calibration.

For all samples the participating laboratories shall apply a method of their choice, taking into account that other PAHs than the four marker PAHs could be present.

Reporting of the results will be open on 8th July 2013. The laboratories shall report the results by **9th September 2013 at the latest** via the ILC web interface using the participation (password) key, shipped together with the test samples (in the same parcel).

### Scoring system

The assigned values will be obtained from the gravimetrical preparation of the materials. They will be verified by chemical analysis.

The target standard deviations will be set:

- for the four individual PAHs as equal to the value derived from the uncertainty function (Uf) according to Commission Regulation (EU) No 836/2011.

- for the sum of the four marker PAHs as equal to the combined standard uncertainty derived from the Uf of the four individual marker PAHs, according to the equation below:

- $Uf(SUM) = \sqrt{U_r^2(BaA) + U_r^2(BaP) + U_r^2(BbF) + U_r^2(CHR)}$

z-scores and zeta(ζ)-scores will be assigned for the marker PAHs (**BaA**, **BaP**, **BbF**, and **CHR**) (see Table 1 for full names) and their sum on the base of the reported final value. For these five measurands a non-reported final value (an empty cell in the reporting system) will be considered as underperformance. In case the content was found to be below the LOD, the scoring will be calculated upon the concentration corresponding to the LOD reported.

**In case of questions please do not hesitate to contact:**

| **PT coordinator** | **Second contact** |
|---|---|
| Stefanka Bratinova<br>Fax: 0032-14-571783<br>e-mail: jrc-irmm-crl-pah@ec.europa.eu | Zuzana Zelinkova |

With kind regards,

Stefanka Bratinova

(on behalf of the Operating Manager of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

Cc: Frans Ferstraete, Michael Flueh, Franz Ulberth, Beatriz de la Calle, Zuzana Zelinkova

INSTRUCTIONS

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 05-07-2013

## Reporting instructions

In the parcel participants will find their **password key** and the **laboratory code** as well as **the link for reporting.** The laboratory code will be used in the report for generating Tables and graphics.

The password key is needed to get access to the interface for reporting of results and for filling in the questionnaire. **All characters of the key should be entered as they are** (e.g. keeping capital letters).

Please remember to save frequently your entries so to avoid any loss of data in case of malfunctioning of the server. **The filling in of all fields marked with a * is mandatory**.

As a support for the reporting steps, PDF preview is available for both data reporting and questionnaire.

The reporting page is structured like a table. To facilitate the compilation of results, it is also possible to download an excel template, in which results may be entered offline. This file has to be saved with a different name on the participant's PC, filled in (without modifying its structure!) and uploaded again in the interface.

After you entered the results directly, or via upload from the Excel table, you still have the possibility to modify entries, if deemed necessary. By clicking on the button "Validate and save" the interface verifies that all mandatory data were correctly entered by the participant.

After having validated all the data, by clicking on the button "Cancel" you are sent to the main page and proceed with the questionnaire.

After having completed the questionnaire and validated it, by clicking on the button "Cancel" you are sent to the main page.

From the main page you can print the PDF of the data entered and decide whether to modify them or to proceed with the **final submission** of your data, by clicking the button "Submit".

You shall then print and sign the final PDF and send it back by fax or by mail to the EU-RL mailbox (jrc-irmm-crl-pah@ec.europa.eu). **Reporting of proficiency test data finishes with sending of the signed printout.**

Retiesweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-crl-pah@ec.europa.eu

*Reporting of RESULTS*

Participants shall report the individual results obtained by replicate analysis (in the web interface labelled as measurement 1/2/3) for the four individual analytes **BaP, BaA, BbF, and CHR** and the final value for proficiency assessment for the 4 individual analytes and the **SUM** parameter. Results have to be reported in **µg/kg and corrected for recovery** and accompanied by their **uncertainty.** In case the content measured should be below the LOD, then the prefix "**<**" shall be entered instead of the default sign = in the field before the result and the numeric value of the **LOD,** expressed in µg/kg, shall be entered.

**IMPORTANT:** the choice of the final value (average of the replicates, robust mean of the **replicates, etc.) is with the participant. Please note that participants will be scored upon** the **final value for the target four marker PAHs and their sum.** Uncertainty has to be reported for the final values only. It has to be reported in µg/kg and should be expressed as **expanded uncertainty with a coverage factor of 2** (it is not necessary to enter the coverage factor k unless it is different from 2).

*Questionnaire*

Participants will be asked to report together with the results also relevant method performance characteristics, a description of the method and of the possible problems encountered when applying their method to this PT samples, and, additionally, some general information on their laboratory.

For the list of questions, please note that if a question mark is displayed beside the question, you can select it to receive additional information on the question and on what the answer should include. Please also note that all fields marked with a * are mandatory.

Concerning the Table of method performances, please follow the following instructions:

- The LOD has to be reported in µg/kg (**IMPORTANT:** check that the LOD entered in this Table is the same as the LOD entered in the results in case the result was entered as < LOD)
- The LOQ has to be reported in µg/kg
- The lower limit of the working range has to be reported in µg/kg
- The higher limit of the working range has to be reported in µg/kg
- The recovery has to be reported in %

SAMPLE RECEIPT

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

**ILC-1061**

**Thirteenth Inter-laboratory comparison study organised by the EU-RL PAHs**

***Analysis of the four marker PAHs in olive oil***

**Confirmation of the receipt of the samples: RECEIPT FORM**

| | |
|---|---|
| **Surname of Participant** | |
| **First name of Participant** | |
| **Institute** | |
| **Address** | |
| **Country** | |

**Content of the parcel**

a) → One amber glass ampoule containing about 20 g of spiked olive oil
b) → One brown glass ampoule with 1 ml standard solution of PAHs in solvent (acetonitrile or toluene) (concentrations known)
c) → A specification sheet for the item b) content (standard solution)
d) → Material safety data sheets for acetonitrile / toluene
e) → One outline of the study and reporting instructions
f) → One paper sheet with the Laboratory ID (assigned for anonymous evaluation of data and for the PT report to be kept for all further communication) and the Password key (for accessing the webpage for reporting data)
g) → One inter-laboratory comparison sample receipt form (= this form)

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Telephone: direct line (32-14) 571 320, Fax: (32-14) 571 783
E-mail: jrc-irmm-crl-pah@ec.europa.eu

**Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:**

| | |
|---|---|
| Date of the receipt of the test materials | |
| All items have been received undamaged | YES……/ NO… |
| If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the numeric code too) | |
| | |
| Please write one item per row | |
| Items are missing | YES……/ NO… |
| If YES, please list missing items according to the letters associated at each item in the list above | |
| | |
| Please write one item per row | |
| Serial number of the spiked olive oil sample you received | |
| Serial number of the standard solution(s) with known concentrations you received | |

Signature:……

**ATTENTION**

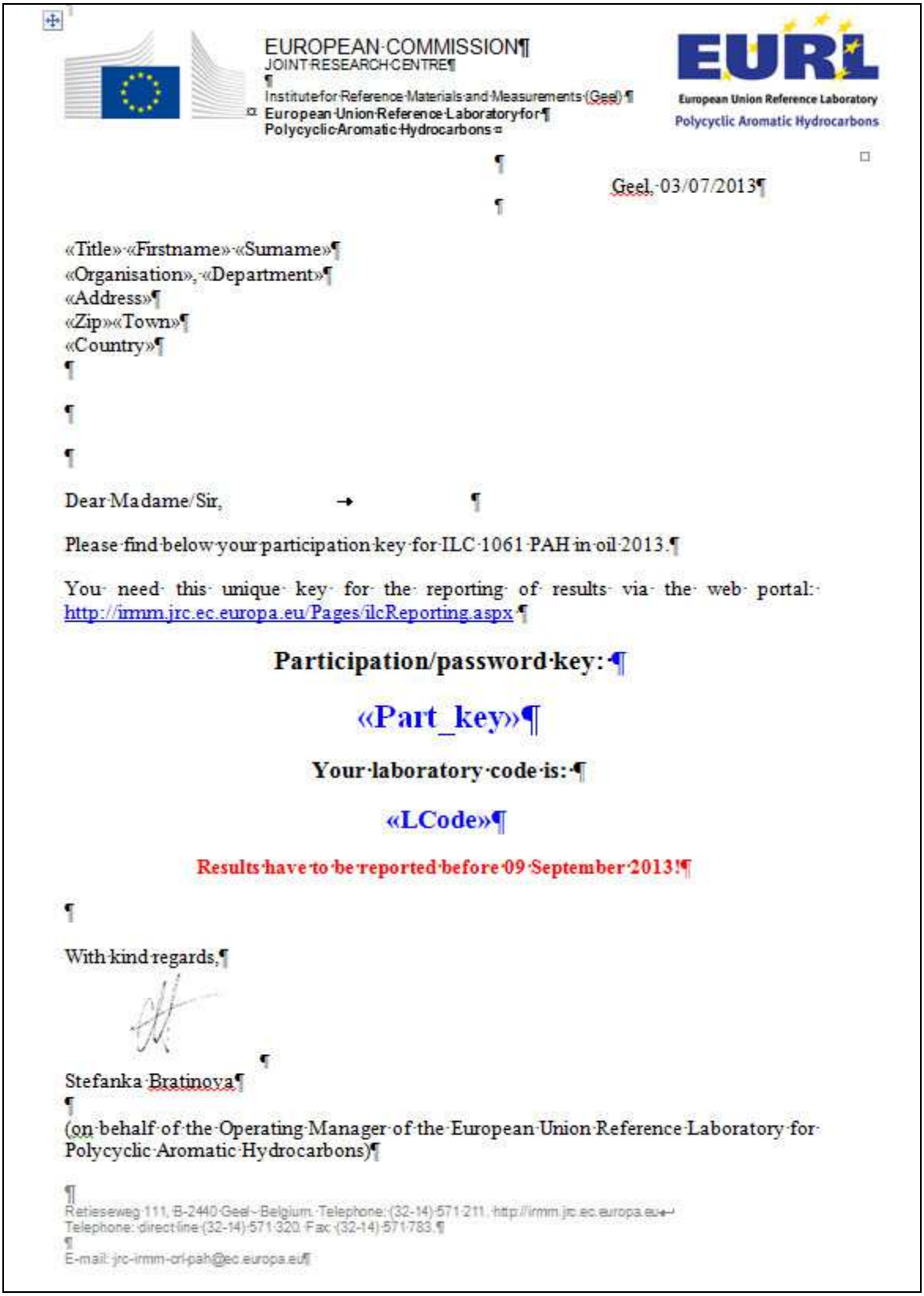
**Please, submit the filled in form by mail to the following address:**

jrc-irmm-eurl-pah@ec.europa.eu

**or print it and send the printout by fax at the attention of Stefanka Bratinova at the following number:**

**+32 – 14 – 571783**

PARTICIPANT CODES



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 03/07/2013

«Title» «Firstname» «Surname»
«Organisation», «Department»
«Address»
«Zip» «Town»
«Country»

Dear Madame/Sir,

Please find below your participation key for ILC 1061 PAH in oil 2013.

You need this unique key for the reporting of results via the web portal: http://irmm.jrc.ec.europa.eu/Pages/ilcReporting.aspx

**Participation/password key:**

**«Part_key»**

**Your laboratory code is:**

**«LCode»**

**Results have to be reported before 09 September 2013!**

With kind regards,

Stefanka Bratinova

(on behalf of the Operating Manager of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-crl-pah@ec.europa.eu

## ANNEX 5: Technical specifications of the calibration solutions

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
**European Union - Reference Laboratory for Polycyclic Aromatic Hydrocarbons**

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 03/07/2013

| **Standard solution specification sheet** | **Product ID: TOL-10/2012-K** |
|---|---|
| Date of production: 24/10/2012 | Total volume: 1 mL |
| Expiry date: *May 2014* | |

**Standard solution composition:**

| | Product name | CAS | Conc.* (ng/g) | Conc.* (ng/ml) | U** ± % |
|---|---|---|---|---|---|
| 1 | Benz[a]anthracene | 56-55-3 | 58.7 | 50.8 | 0.39 |
| 2 | Benzo[a]pyrene | 50-32-8 | 58.3 | 50.4 | 0.53 |
| 3 | Benzo[b]fluoranthene | 205-99-2 | 58.4 | 50.5 | 0.87 |
| 4 | Chrysene | 218-01-9 | 58.5 | 50.6 | 0.83 |
| 5 | SUM PAH4 | | 234.0 | 202.3 | 1.37 |

** The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

**Solvent: Toluene**

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-crl-pah@ec.europa.eu

EUROPEAN COMMISSION
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Institute for Reference Materials and Measurements
**European Union - Reference Laboratory for Polycyclic Aromatic Hydrocarbons**

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 03.07.2013

| **Standard solution specification sheet** | **Product ID: ACN-10/2012-K** |
|---|---|
| Date of production: 24/10/2012 | Total volume: 1 mL |
| Expiry date: *May 2014* | |

**Standard solution composition:**

| | Product name | CAS | Conc.* (ng/g) | Conc.* (ng/ml) | U** ± % |
|---|---|---|---|---|---|
| 1 | Benz[a]anthracene | 56-55-3 | 64.1 | 50.0 | 0.39 |
| 2 | Benzo[a]pyrene | 50-32-8 | 63.6 | 49.6 | 0.53 |
| 3 | Benzo[b]fluoranthene | 205-99-2 | 63.8 | 49.7 | 0.87 |
| 4 | Chrysene | 218-01-9 | 63.9 | 49.8 | 0.83 |
| 5 | SUM PAH4 | | 255.3 | 199.2 | 1.37 |

** The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

**Solvent: Acetonitrile : Toluene (m:m, 99.4: 0.6)**

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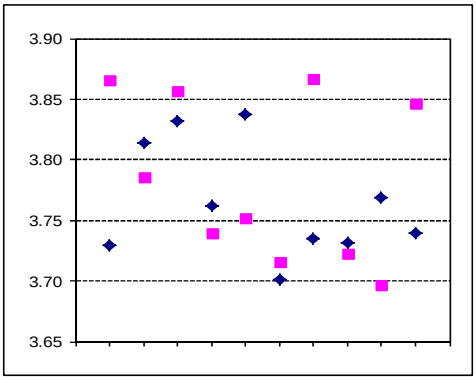
## ANNEX 6: Homogeneity of the test material

Analyte: **BAA**

| | | | | |
|---|---|---|---|---|
| | **n =** | 10 | | |
| | **mean =** | 3.7749 | 22% | = **σ-trg(%)** |
| 0.00181421 | **$s_x$ =** | 0.0426 | 0.8305 | = **σ-trg** |
| √MSW = | **$s_w$ =** | 0.0556 | | |
| | **$s_s$ =** | 0.0164 | 0.2491 | = **0,3*s** |

| | | | |
|---|---|---|---|
| ISO-13528 | passed | | |
| F = | 1.17507595 | 3.02038295 | = Fcrit |
| | passed | | |
| IUPAC | | | |
| (MSB-MSW)/2 | 0.0003 | 0.1198 | = F1*(0,3*s)$^2$+F2*MSW |
| | passed | | |

| Bottle | Result a | Result b | diff | sum | avg |
|---|---|---|---|---|---|
| Ampoule 11 | 3.73 | 3.87 | -0.14 | 7.60 | 3.80 |
| Ampoule 21 | 3.81 | 3.79 | 0.03 | 7.60 | 3.80 |
| Ampoule 29 | 3.83 | 3.86 | -0.02 | 7.69 | 3.84 |
| Ampoule 47 | 3.76 | 3.74 | 0.02 | 7.50 | 3.75 |
| Ampoule 56 | 3.84 | 3.75 | 0.09 | 7.59 | 3.79 |
| Ampoule 63 | 3.70 | 3.72 | -0.02 | 7.42 | 3.71 |
| Ampoule 72 | 3.73 | 3.87 | -0.13 | 7.60 | 3.80 |
| Ampoule 89 | 3.73 | 3.72 | 0.01 | 7.45 | 3.73 |
| Ampoule 102 | 3.77 | 3.70 | 0.07 | 7.47 | 3.73 |
| Ampoule 120 | 3.74 | 3.85 | -0.11 | 7.59 | 3.79 |




$\sum$**(diff)$^2$** = 0.06175636

var(sum)/2 = 0.00363 =MSB

## Stability Study for : BAA

**Data for T= 22°C, Treference - 0°C**

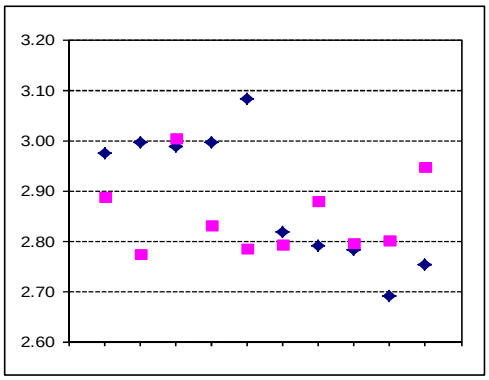
| | | | |
|---|---|---|---|
| DATASET PROPERTIES | | | Shelf Life / Uncertainty Estimation |
| # of Determinations = | 12 | | CALCULATION OF Ults for given Xshelf |
| Average of Dataset = | 3.757 | | Given Xshelf = 10 Weeks |
| R.S.D. of Average(%) = | 1.281 | | U_b =0.003 |
| R.S.E. of Average(%) = | 0.37 | | |
| StDev of Average = | 0.048 | | Ults = 0.028 |
| S.E. of Average = | 0.014 | | Ults[%] = 0.7% |
| REGRESSION LINE PARAMETERS | | | |
| Slope = | 0 | | |
| SE Slope = | 0.003 | | |
| Intercept = | 3.757 | | |
| SE Intercept = | 0.021 | | |
| Correlation Coefficient = | 0 | | |
| Slope of the linear regression significantly <> 0 (95%) : | No | | |
| Slope of the linear regression significantly <> 0 (99%) : | No | | |

Analyte: **BAP**

| | | | | |
|---|---|---|---|---|
| | **n =** | 10 | | |
| | **mean =** | 2.8687 | 22% | = **σ-trg(%)** |
| 0.005939217 | $s_x$ = | 0.0771 | 0.6311 | = **σ-trg** |
| √MSW = | $s_w$ = | 0.1073 | | |
| | $s_s$ = | 0.0133 | 0.1893 | = **0,3*s** |

| | | | |
|---|---|---|---|
| ISO-13528 | passed | | |
| F = | 1.03080074 | 3.02038295 | = Fcrit |
| | passed | | |
| IUPAC | | | |
| (MSB-MSW)/2 | 0.0002 | 0.0790 | = F1*(0,3*s)$^2$+F2*MSW |
| | passed | | |

| Bottle | Result a | Result b | diff | sum | avg |
|---|---|---|---|---|---|
| Ampoule 11 | 2.97 | 2.89 | 0.09 | 5.86 | 2.93 |
| Ampoule 21 | 3.00 | 2.77 | 0.22 | 5.77 | 2.89 |
| Ampoule 29 | 2.99 | 3.00 | -0.02 | 5.99 | 3.00 |
| Ampoule 47 | 3.00 | 2.83 | 0.17 | 5.83 | 2.91 |
| Ampoule 56 | 3.08 | 2.79 | 0.29 | 5.87 | 2.93 |
| Ampoule 63 | 2.82 | 2.79 | 0.02 | 5.61 | 2.81 |
| Ampoule 72 | 2.79 | 2.88 | -0.09 | 5.67 | 2.84 |
| Ampoule 89 | 2.78 | 2.80 | -0.01 | 5.58 | 2.79 |
| Ampoule 102 | 2.69 | 2.80 | -0.11 | 5.49 | 2.75 |
| Ampoule 120 | 2.75 | 2.95 | -0.20 | 5.70 | 2.85 |




$\sum$**(diff)**$^2$ = 0.23047005

var(sum)/2 = 0.01188 =MSB

## Stability Study for : BAP

**Data for T= 22°C, Treference - 0°C**

| DATASET PROPERTIES | | Shelf Life / Uncertainty Estimation |
|---|---|---|
| # of Determinations = | 18 | CALCULATION OF Ults for given Xshelf |
| Average of Dataset = | 2.876 | Given Xshelf = 10 Weeks |
| R.S.D. of Average(%) = | 1.496 | U_b =0.002 |
| R.S.E. of Average(%) = | 0.353 | |
| StDev of Average = | 0.043 | Ults = 0.025 |
| S.E. of Average = | 0.01 | Ults[%] = 0.9% |
| REGRESSION LINE PARAMETERS | | |
| Slope = | 0.004 | |
| SE Slope = | 0.002 | |
| Intercept = | 2.858 | |
| SE Intercept = | 0.016 | |
| Correlation Coefficient = | 0.117 | |
| Slope of the linear regression significantly <> 0 (95%) : | No | |
| Slope of the linear regression significantly <> 0 (99%) : | No | |

Analyte: **BBF**

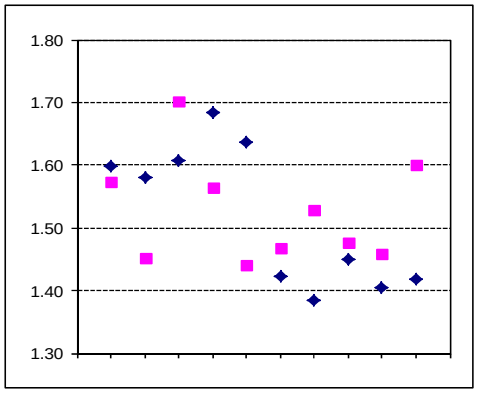
| | | | | |
|---|---|---|---|---|
| | **n =** | 10 | | |
| | **mean =** | 1.5225 | 22% | = **σ-trg(%)** |
| 0.006059358 | $s_x$ = | 0.0778 | 0.3350 | = **σ-trg** |
| √MSW = | $s_w$ = | 0.0834 | | |
| | $s_s$ = | 0.0508 | 0.1005 | = **0,3*s** |

| | | | |
|---|---|---|---|
| ISO-13528 | passed | | |
| F = | 1.74417084 | 3.02038295 | = Fcrit |
| | passed | | |
| IUPAC | | | |
| (MSB-MSW)/2 | 0.0026 | 0.0260 | = F1*(0,3*s)$^2$+F2*MSW |
| | passed | | |

| Bottle | Result a | Result b | diff | sum | avg |
|---|---|---|---|---|---|
| Ampoule 11 | 1.60 | 1.57 | 0.02 | 3.17 | 1.59 |
| Ampoule 21 | 1.58 | 1.45 | 0.13 | 3.03 | 1.52 |
| Ampoule 29 | 1.61 | 1.70 | -0.10 | 3.31 | 1.65 |
| Ampoule 47 | 1.68 | 1.56 | 0.12 | 3.25 | 1.62 |
| Ampoule 56 | 1.64 | 1.44 | 0.20 | 3.08 | 1.54 |
| Ampoule 63 | 1.42 | 1.47 | -0.04 | 2.89 | 1.44 |
| Ampoule 72 | 1.38 | 1.53 | -0.14 | 2.91 | 1.46 |
| Ampoule 89 | 1.45 | 1.48 | -0.03 | 2.92 | 1.46 |
| Ampoule 102 | 1.41 | 1.46 | -0.05 | 2.86 | 1.43 |
| Ampoule 120 | 1.42 | 1.60 | -0.18 | 3.02 | 1.51 |

$\sum$**(diff)**$^2$ = 0.13896248

var(sum)/2 = 0.01212 =MSB




## Stability Study for : BAP

**Data for T= 22°C, Treference - 0°C**

| | | | |
|---|---|---|---|
| ========== | | | ========== |
| DATASET PROPERTIES | | | Shelf Life / Uncertainty Estimation |
| # of Determinations = | 18 | | CALCULATION OF Ults for given Xshelf |
| Average of Dataset = | 1.389 | | Given Xshelf = 10 Weeks |
| R.S.D. of Average(%) = | 2.681 | | U_b =0.002 |
| R.S.E. of Average(%) = | 0.632 | | |
| StDev of Average = | 0.037 | | Ults = 0.022 |
| S.E. of Average = | 0.009 | | Ults[%] = 1.5% |
| | | | ========== |
| ========== | | | |
| REGRESSION LINE PARAMETERS | | | |
| Slope = | 0.002 | | |
| SE Slope = | 0.002 | | |
| Intercept = | 1.38 | | |
| SE Intercept = | 0.014 | | |
| Correlation Coefficient = | 0.043 | | |
| Slope of the linear regression significantly <> 0 (95%) : | No | | |
| Slope of the linear regression significantly <> 0 (99%) : | No | | |

Analyte: **CHR**

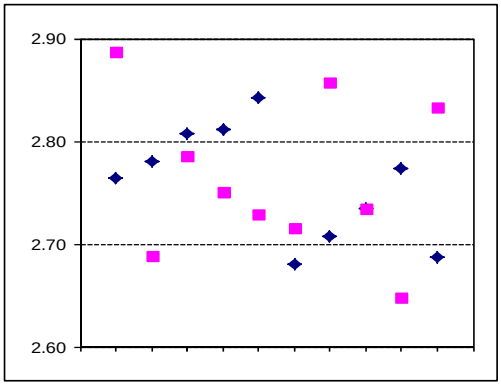
| | | | | |
|---|---|---|---|---|
| | **n =** | 10 | | |
| | **mean =** | 2.7609 | 22% | = **σ-trg(%)** |
| 0.001651503 | **$s_x$ =** | 0.0406 | 0.6074 | = **σ-trg** |
| √MSW = | **$s_w$ =** | 0.0712 | | |
| | **$s_s$ =** | 0.0298 | 0.1822 | = **0,3*s** |

| | | | |
|---|---|---|---|
| ISO-13528 | passed | | |
| F = | 0.65075845 | 3.02038295 | = Fcrit |
| | passed | | |
| IUPAC | | | |
| (MSB-MSW)/2 | -0.0009 | 0.0675 | = F1*(0,3*s)$^2$+F2*MSW |
| | passed | | |

| Bottle | Result a | Result b | diff | sum | avg |
|---|---|---|---|---|---|
| Ampoule 11 | 2.76 | 2.89 | -0.12 | 5.65 | 2.83 |
| Ampoule 21 | 2.78 | 2.69 | 0.09 | 5.47 | 2.73 |
| Ampoule 29 | 2.81 | 2.79 | 0.02 | 5.59 | 2.80 |
| Ampoule 47 | 2.81 | 2.75 | 0.06 | 5.56 | 2.78 |
| Ampoule 56 | 2.84 | 2.73 | 0.11 | 5.57 | 2.79 |
| Ampoule 63 | 2.68 | 2.71 | -0.03 | 5.40 | 2.70 |
| Ampoule 72 | 2.71 | 2.86 | -0.15 | 5.57 | 2.78 |
| Ampoule 89 | 2.73 | 2.73 | 0.00 | 5.47 | 2.73 |
| Ampoule 102 | 2.77 | 2.65 | 0.13 | 5.42 | 2.71 |
| Ampoule 120 | 2.69 | 2.83 | -0.15 | 5.52 | 2.76 |

**∑(diff)$^2$ =** 0.10151251

var(sum)/2 = 0.00330 =MSB




## Stability Study for : CHR

**Data for T= 22°C, Treference - 0°C**

| **DATASET PROPERTIES** | | **Shelf Life / Uncertainty Estimation** |
|---|---|---|
| # of Determinations = | 18 | CALCULATION OF Ults for given Xshelf |
| Average of Dataset = | 2.509 | Given Xshelf = 10 Weeks |
| R.S.D. of Average(%) = | 1.731 | U_b =0.003 |
| R.S.E. of Average(%) = | 0.408 | |
| StDev of Average = | 0.043 | Ults = 0.025 |
| S.E. of Average = | 0.01 | Ults[%] = 1.0% |

| **REGRESSION LINE PARAMETERS** | |
|---|---|
| Slope = | -0.001 |
| SE Slope = | 0.003 |
| Intercept = | 2.514 |
| SE Intercept = | 0.017 |
| Correlation Coefficient = | 0.006 |
| Slope of the linear regression significantly <> 0 (95%) : | No |
| Slope of the linear regression significantly <> 0 (99%) : | No |

## ANNEX 7: Questionnaire

BLANK TEMPLATE

1. **Did you find the instructions distributed for this PT adequate?** *
- ◯ a) Yes
- ◯ b) No

1.1. If NO, please report about possible lacking information *

2. **Did you experience any specific problem related to the organisation of this PT?**
- ◯ a) yes
- ◯ b) no

2.1. If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc) *

3. **Did your laboratory quantify PAHs in EDIBLE OIL before?** *
- ◯ a) yes
- ◯ b) no

3.1. If YES, for how long? (expressed in years) *
- ◯ a) <1
- ◯ b) 1-4
- ◯ c) 4-8
- ◯ d) 8-15
- ◯ e) >15
- ◯ f) other

3.1.1. If OTHER, please specify *

3.2. If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? *
- ◯ a) < 10
- ◯ b) 10-50
- ◯ c) 50-100
- ◯ d) > 100
- ◯ e) other

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3.2.1. If OTHER, please specify *

4. **Is your laboratory accredited for the determination of PAHs in food?** *
- ◯ a) yes
- ◯ b) no

4.1. If YES, please specify the food matrix included in the accreditation scope *
- ◯ a) Oils and fats (6.1.1)
- ◯ b) Smoked meats and smoked meat products (6.1.2)
- ◯ c) Muscle meat of smoked fish and smoked fishery products (6.1.3)
- ◯ d) Muscle meat of fish (6.1.4)
- ◯ e) Crustaceans, cephalopods, other than smoked (6.1.5)
- ◯ f) Bivalve molluscs (6.1.6)
- ◯ g) Processed cereal-based foods and baby foods for infants and young (6.1.7)
- ◯ h) Infant formulae and follow-on formulae (6.1.8)
- ◯ i) Dietary foods for special medical purposes (6.1.9)
- ◯ j) OTHER
- ◯ k) All the matrices listed above
- ◯ l) the following of the matrices listed above

4.1.1. If OTHER, please specify *

4.1.2. If you chose "the following of the matrices listed above", please report the corresponding codes *

4.2. If YES, please specify the PAHs included in the accreditation scope *
- ◯ a) BaP
- ◯ b) 4 marker PAHs
- ◯ c) 15+1 EU priority PAHs
- ◯ d) 16 EPA PAHs
- ◯ e) other

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4.2.1. If OTHER, please specify *

5. **How did you prepare the sample?** *

- a) Dilution
- b) No preparation
- c) Other

5.1. If OTHER, please describe *

6. **Which extraction method did you use?** *

- a) Saponification
- b) Pressurized liquid extraction
- c) Soxhlet extraction
- d) No extraction
- e) Other

6.1. If OTHER, please describe *

7. **Which was the MAIN purification step of your method?** *

- a) Donor-Acceptor Complex Chromatography (DACC)
- b) Size-Exclusion Chromatography
- c) Solid Phase Extraction (SPE)
- d) Solvent partitioning
- e) Other

7.1. If OTHER, please describe *



8. **Which was the instrumental detection method you applied?** *

- a) HPLC-FLD
- b) UHPLC-FLD
- c) HPLC-FLD-UV
- d) UHPLC-FLD-UV
- e) HPLC-MS
- f) UHPLC-MS
- g) HPLC-MS/MS
- h) UHPLC-MS/MS
- i) GC-FID
- j) GC-MS
- k) GC-HRMS
- l) GC-MS/MS
- m) Other

8.1. If OTHER, please describe *

9. **In case you applied a gaschromatographic technique, please describe the analytical column used (stationary phase, length, internal diameter, film thickness)**

10. **In case you applied a liquid chromatographic technique, please describe the analytical column used (stationary phase, particle size, length, internal diameter)**

11. **Did you encounter any problems during the analysis of the sample?** *

- a) Yes
- b) No

11.1. If YES, please describe *

12. **In the following field you may add any further information about this PT and the analysis of the samples**

METHOD PERFORMANCE PARAMETERS

With reference to Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011, non-compliant method performance characteristics are marked in the tables in bold red font. Threshold values for the evaluation were LOD ≤ 0.30 µg/kg, LOQ ≤ 0.90 µg/kg, and recovery outside the range of 50 % - 120 %. Levels of the lower limit of the working range, which are lower than LOQ, are marked with yellow, while those lower than LOD are marked by bold red font.

Method performance data reported by participants for the determination of BAA

| LCode | Measurand | LOD [µg/kg] | LOQ [µg/kg] | Recovery [%] | Linear working range lower limit [µg/kg] | Linear working range higher limit [µg/kg] |
|---|---|---|---|---|---|---|
| 101 | BaA | 0.01 | 0.01 | 72 | **0.005** | 100 |
| 102 | BaA | 0.1 | 0.3 | 73 | 0.1 | 40 |
| 103 | BaA | 0.007 | 0.4 | 97.3 | 0.06 | 10 |
| 104 | BaA | **0.5** | **1** | 107 | 0.5 | 40 |
| 105 | BaA | 0.07 | 0.21 | 95 | 0.21 | 20 |
| 106 | BaA | 0.11 | 0.21 | 93.8 | 0.5 | 20 |
| 107 | BaA | 0.25 | 0.75 | | 0.75 | 375 |
| 108 | BaA | 0.01 | 0.02 | 66 | 0.02 | 30 |
| 109 | BaA | n.r. | n.r. | n.r. | n.r. | n.r. |
| 110 | BaA | 0.05 | 0.16 | 96 | 0.1 | 10 |
| 111 | BaA | 0.06 | 0.2 | 100.9 | **0.03** | 13 |
| 112 | BaA | 0.07 | 0.2 | 85 | 0.2 | 10 |
| 113 | BaA | 0.3 | 0.9 | 97 | **0.1** | 20 |
| 114 | BaA | 0.13 | 0.4 | 91 | 0.4 | 100 |
| 115 | BaA | 0.1 | 0.5 | 90 | 0.5 | 25 |
| 116 | BaA | 0.2 | 0.6 | 120 | 0.4 | 8 |
| 117 | BaA | 0.06 | 0.21 | 89 | 1 | 20 |
| 118 | BaA | 0.01 | 0.03 | 83 | 0.1 | 40 |
| 119 | BaA | 0.3 | 0.8 | 94 | 1 | 24 |
| 120 | BaA | 0.3 | 0.5 | 86 | 0.25 | 50 |
| 121 | BaA | 0.2 | 0.6 | 100 | 0.2 | 20 |
| 122 | BaA | n.r. | n.r. | n.r. | n.r. | n.r. |
| 123 | BaA | 0.025 | 0.05 | 105 | 0.05 | 10 |
| 124 | BaA | 0.21 | 0.69 | 91.4 | 0.4 | 50 |
| 125 | BaA | 0.2 | 0.4 | 102 | 0.5 | 25 |
| 126 | BaA | 0.5 | 1 | 100 | | |
| 501 | BaA | 0.2 | 0.8 | 109 | 0.8 | 12.5 |
| 502 | BaA | n.r. | n.r. | n.r. | n.r. | n.r. |
| 503 | BaA | 0.21 | 0.42 | 98 | 0.47 | 32 |
| 504 | BaA | 0.26 | 0.3 | 75-110 | | |
| 505 | BaA | 0.2 | 0.2 | 79 | 0.2 | 4.5 |
| 506 | BaA | 0.1 | 0.3 | 75 | | |
| 507 | BaA | 0.3 | 0.9 | 131 | 0.9 | 50 |
| 508 | BaA | 0.05 | 0.1 | 80 | | |
| 509 | BaA | 0.07 | 0.21 | 105 | | |
| 510 | BaA | 0.1 | 0.3 | 105 | 0.5 | 10 |

n.r.: not reported

Method performance data reported by participants for the determination of BAP

| Lcode | Measurand | LOD [µg/kg] | LOQ [µg/kg] | Recovery [%] | Linear working range lower limit [µg/kg] | Linear working range higher limit [µg/kg] |
|---|---|---|---|---|---|---|
| 101 | BaP | 0.08 | 0.08 | 60 | 0.005 | 100 |
| 102 | BaP | 0.1 | 0.3 | 67 | 0.1 | 40 |
| 103 | BaP | 0.003 | 0.41 | 101.7 | 0.06 | 9.92 |
| 104 | BaP | 0.5 | 1 | 116 | 0.5 | 40 |
| 105 | BaP | 0.05 | 0.15 | 96 | 0.15 | 20 |
| 106 | BaP | 0.09 | 0.18 | 88.7 | 0.5 | 20 |
| 107 | BaP | 0.25 | 0.75 | n.r. | 0.75 | 375 |
| 108 | BaP | 0.01 | 0.02 | 54 | 0.02 | 30 |
| 109 | BaP | n.r. | n.r. | n.r. | n.r. | n.r. |
| 110 | BaP | 0.11 | 0.38 | 102 | 0.1 | 10 |
| 111 | BaP | 0.06 | 0.2 | 84.5 | 0.03 | 13 |
| 112 | BaP | 0.07 | 0.2 | 93 | 0.2 | 10 |
| 113 | BaP | 0.3 | 0.9 | 97 | 0.1 | 20 |
| 114 | BaP | 0.16 | 0.53 | 93 | 0.4 | 100 |
| 115 | BaP | 0.04 | 0.2 | 90 | 0.2 | 10 |
| 116 | BaP | 0.1 | 0.3 | 104 | 0.4 | 8 |
| 117 | BaP | 0.04 | 0.14 | 77 | 1 | 20 |
| 118 | BaP | 0.01 | 0.03 | 82 | 0.1 | 40 |
| 119 | BaP | 0.3 | 0.8 | 95 | 1 | 24 |
| 120 | BaP | 0.3 | 0.5 | 90 | 0.25 | 50 |
| 121 | BaP | 0.2 | 0.6 | 90 | 0.2 | 20 |
| 122 | BaP | n.r. | n.r. | n.r. | n.r. | n.r. |
| 123 | BaP | 0.025 | 0.05 | 107 | 0.05 | 10 |
| 124 | BaP | 0.16 | 0.53 | 70.3 | 0.4 | 50 |
| 125 | BaP | 0.2 | 0.4 | 100 | 0.5 | 25 |
| 126 | BaP | 0.2 | 0.4 | 100 | | |
| 501 | BaP | 0.2 | 0.8 | 102 | 0.8 | 12.5 |
| 502 | BaP | n.r. | n.r. | n.r. | n.r. | n.r. |
| 503 | BaP | 0.09 | 0.18 | 94 | 0.55 | 32 |
| 504 | BaP | 0.29 | 0.5 | 75-110 | | |
| 505 | BaP | 0.2 | 0.2 | 94 | 0.2 | 4.5 |
| 506 | BaP | 0.1 | 0.3 | 70 | | |
| 507 | BaP | 0.3 | 0.9 | 114 | 0.9 | 50 |
| 508 | BaP | 0.05 | 0.1 | 88 | | |
| 509 | BaP | 0.08 | 0.24 | 101 | | |
| 510 | BaP | 0.1 | 0.3 | 105 | 0.5 | 10 |

n.r.: not reported

Method performance data reported by participants for the determination of BBF

| LCode | Measurand | LOD [µg/kg] | LOQ [µg/kg] | Recovery [%] | Linear working range lower limit [µg/kg] | Linear working range higher limit [µg/kg] |
|---|---|---|---|---|---|---|
| 101 | BbF | 0.06 | 0.06 | 62 | 0.005 | 100 |
| 102 | BbF | 0.1 | 0.3 | 70 | 0.1 | 40 |
| 103 | BbF | 0.014 | 0.41 | 95.3 | 0.06 | 9.94 |
| 104 | BbF | 0.5 | 1 | 106 | 0.5 | 40 |
| 105 | BbF | 0.15 | 0.45 | 95 | 0.45 | 40 |
| 106 | BbF | 0.21 | 0.41 | 91.6 | 0.5 | 20 |
| 107 | BbF | 0.25 | 0.75 | n.r. | 0.75 | 375 |
| 108 | BbF | 0.01 | 0.02 | 54 | 0.02 | 30 |
| 109 | BbF | n.r. | n.r. | n.r. | n.r. | n.r. |
| 110 | BbF | 0.11 | 0.37 | 118 | 0.1 | 10 |
| 111 | BbF | 0.06 | 0.2 | 86 | 0.03 | 13 |
| 112 | BbF | 0.07 | 0.2 | 102 | 0.2 | 10 |
| 113 | BbF | 0.3 | 0.9 | 96 | 0.1 | 20 |
| 114 | BbF | 0.14 | 0.4 | 99 | 0.4 | 100 |
| 115 | BbF | 0.04 | 0.2 | 90 | 0.2 | 10 |
| 116 | BbF | 0.3 | 0.9 | 112 | 0.4 | 8 |
| 117 | BbF | 0.23 | 0.75 | 82 | 1 | 20 |
| 118 | BbF | 0.01 | 0.03 | 80 | 0.1 | 40 |
| 119 | BbF | 0.3 | 0.8 | 88 | 1 | 24 |
| 120 | BbF | 0.3 | 0.5 | 92 | 0.25 | 50 |
| 121 | BbF | 0.2 | 0.6 | 101 | 0.2 | 20 |
| 122 | BbF | n.r. | n.r. | n.r. | n.r. | n.r. |
| 123 | BbF | 0.05 | 0.1 | 98 | 0.1 | 10 |
| 124 | BbF | 0.19 | 0.63 | 80.3 | 0.4 | 50 |
| 125 | BbF | 0.2 | 0.4 | 99 | 0.5 | 25 |
| 126 | BbF | 0.2 | 0.4 | 100 | | |
| 501 | BbF | 0.2 | 0.8 | 90 | 0.8 | 12.5 |
| 502 | BbF | n.r. | n.r. | n.r. | n.r. | n.r. |
| 503 | BbF | 0.18 | 0.36 | 94 | 0.78 | 32 |
| 504 | BbF | 0.26 | 0.3 | 60-115 | | |
| 505 | BbF | 0.2 | 0.2 | 84 | 0.2 | 4.5 |
| 506 | BbF | 0.1 | 0.3 | 80 | | |
| 507 | BbF | 0.3 | 0.9 | 100 | 0.9 | 50 |
| 508 | BbF | 0.05 | 0.1 | 90 | | |
| 509 | BbF | 0.15 | 0.45 | 100 | | |
| 510 | BbF | 0.1 | 0.3 | 95 | 0.5 | 10 |

n.r.: not reported

Method performance data reported by participants for the determination of CHR

| LCode | Measurand | LOD [µg/kg] | LOQ [µg/kg] | Recovery [%] | Linear working range lower limit [µg/kg] | Linear working range higher limit [µg/kg] |
|---|---|---|---|---|---|---|
| 101 | CHR | 0.04 | 0.04 | 69 | 0.005 | 100 |
| 102 | CHR | 0.1 | 0.3 | 71 | 0.1 | 40 |
| 103 | CHR | 0.007 | 0.41 | 97.3 | 0.06 | 9.96 |
| 104 | CHR | 0.5 | 1 | 103 | 0.5 | 40 |
| 105 | CHR | 0.03 | 0.09 | 96 | 0.09 | 20 |
| 106 | CHR | 0.11 | 0.22 | 87.9 | 0.5 | 20 |
| 107 | CHR | 0.25 | 0.75 | n.r. | 0.75 | 375 |
| 108 | CHR | 0.01 | 0.02 | 52 | 0.02 | 30 |
| 109 | CHR | n.r. | n.r. | n.r. | n.r. | n.r. |
| 110 | CHR | 0.04 | 0.12 | 97 | 0.1 | 10 |
| 111 | CHR | 0.2 | 0.5 | 100.7 | 0.03 | 13 |
| 112 | CHR | 0.07 | 0.2 | 90 | 0.2 | 10 |
| 113 | CHR | 0.3 | 0.9 | 100 | 0.1 | 20 |
| 114 | CHR | 0.12 | 0.4 | 105 | 0.4 | 100 |
| 115 | CHR | 0.1 | 0.5 | 90 | 0.5 | 25 |
| 116 | CHR | 0.3 | 0.9 | 100 | 0.4 | 8 |
| 117 | CHR | 0.01 | 0.03 | 90 | 1 | 20 |
| 118 | CHR | 0.01 | 0.03 | 79 | 0.1 | 40 |
| 119 | CHR | 0.3 | 0.8 | 88 | 1 | 24 |
| 120 | CHR | 0.3 | 0.5 | 93 | 0.25 | 50 |
| 121 | CHR | 0.2 | 0.6 | 113 | 0.2 | 20 |
| 122 | CHR | n.r. | n.r. | n.r. | n.r. | n.r. |
| 123 | CHR | 0.025 | 0.05 | 105 | 0.05 | 10 |
| 124 | CHR | 0.32 | 1.05 | 77.7 | 0.4 | 50 |
| 125 | CHR | 0.2 | 0.4 | 107 | 0.5 | 25 |
| 126 | CHR | 1 | 2 | 100 | | |
| 501 | CHR | 0.2 | 0.8 | 100 | 0.8 | 12.5 |
| 502 | CHR | n.r. | n.r. | n.r. | n.r. | n.r. |
| 503 | CHR | 0.38 | 0.72 | 94 | 0.58 | 32 |
| 504 | CHR | 0.19 | 0.2 | 60-115 | | |
| 505 | CHR | 0.2 | 0.2 | 79 | 0.2 | 4.5 |
| 506 | CHR | 0.1 | 0.3 | 75 | | |
| 507 | CHR | 0.3 | 0.9 | 102 | 0.9 | 50 |
| 508 | CHR | 0.05 | 0.1 | 77 | | |
| 509 | CHR | 0.04 | 0.12 | 93 | | |
| 510 | CHR | 0.1 | 0.3 | 95 | 0.5 | 10 |

n.r.: not reported

QUESTIONNAIRE:

**On the organisation of the PT**

- Did you find the instructions distributed for this PT adequate?
- If NO, please report about possible lacking information (for NRLs no matching case)
- Did you experience any specific problem related to the organization of this PT?
- If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc)

**On participants profile**

- Did your laboratory quantify PAHs in EDIBLE OIL before?
- If YES, for how long? (expressed in years) - If OTHER, please specify
- If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? - If OTHER, please specify
- Is your laboratory accredited for the determination of PAHs in food?
- If YES, please specify the food matrix included in the accreditation scope - If OTHER, please specify - If you chose "the following of the matrices listed above", please report the corresponding codes
- If YES, please specify the PAHs included in the accreditation scope - If OTHER, please specify

| Lab Code | Adequate instruct-tions | Specific pro-blem | Analysis before | Accredited for PAH in food | For how long, years | how many samples/ per year | Matrices accredited | PAH in the scope |
|---|---|---|---|---|---|---|---|---|
| 101 | a) Yes | b) no | a) yes | a) yes | e) >15 | b) 10-50 | k) All the matrices listed above | 28 PAHs including the above |
| 102 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | b) 10-50 | k) All the matrices listed above | 15 EU PAHs (not BcL),phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, perylene, bens(e)pyrene, anthanthrene, coronene |
| 103 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | Very variable at year level | k) All the matrices listed above | 15 EU markers PAHs (No CPP) |
| 104 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | c) 50-100 | a) Oils and fats (6.1.1) | c) 15+1 EU markers PAHs |
| 105 | a) Yes | b) no | a) yes | a) yes | e) >15 | c) 50-100 | 6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8 | c) 15+1 EU markers PAHs |
| 106 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50, in 2009 >100 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 107 | a) Yes | b) no | a) yes | a) yes | b) 1-4 | a) < 10 | (6.1.1) (6.1.4) (6.1.6) | c) 15+1 EU markers PAHs |
| 108 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | b) 10-50 | a) Oils and fats (6.1.1) | c) 15+1 EU markers PAHs |
| 110 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | a) < 10 | 6.1.1, 6.1.2, 6.1.3 | b) 4 marker PAHs |
| 111 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | c) 50-100 | 6.1.1, 6.1.3, 6.1.4 | a) BaP |
| 112 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | b) 10-50 | a) Oils and fats (6.1.1) | b) 4 marker PAHs |
| 113 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50 | Categories a, b, c, d, g & h + supplements, herbs & spices, cocoa, tea & coffee | EU markers 15 |
| 114 | a) Yes | * | a) yes | a) yes | c) 4-8 | b) 10-50 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 115 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | a) < 10 | a) Oils and fats (6.1.1) | b) 4 marker PAHs |
| 116 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | b) 10-50 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 117 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50 | a,b,c,d,f,g,h, | c) 15+1 EU markers PAHs |
| 118 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | a) < 10 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 119 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | a) < 10 | 6.1.1, 6.1.2 and 6.1.3 | b) 4 marker PAHs |
| 120 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | a) < 10 | a, b, c, g, h | c) 15+1 EU markers PAHs |

| Lab Code | Adequate instruct-tions | Specific pro-blem | Analysis before | Accredited for PAH in food | For how long, years | how many samples/ per year | Matrices accredited | PAH in the scope |
|---|---|---|---|---|---|---|---|---|
| 121 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | start 20 samples, now <10 per year | 6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.6, 6.1.7, 6.1.8 | acenaphthene, anthracene, fluorene, fluoranthene, pyrene, benzo[e]pyrene, phenanthrene, acenaphthylene, 15+1 EU markers PAHs |
| 123 | a) Yes | b) no | a) yes | a) yes | d) 8-15 | d) > 100 | 6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8 | c) 15+1 EU markers PAHs |
| 124 | a) Yes | b) no | a) yes | b) no | c) 4-8 | b) 10-50 | true | true |
| 125 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | a) < 10 | a) Oils and fats (6.1.1) | b) 4 marker PAHs |
| 126 | a) Yes | b) no | a) yes | b) no | only for BaP | b) 10-50 | b) (6.1.2) | only Benzo(a)pyrene |
| 501 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 503 | a) Yes | b) no | a) yes | a) yes | b) 1-4 | c) 50-100 | a) Oils and fats (6.1.1) | a) BaP |
| 504 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | d) > 100 | a) Oils and fats (6.1.1) | c) 15+1 EU markers PAHs |
| 505 | a) Yes | b) no | a) yes | a) yes | b) 1-4 | b) 10-50 | a) Oils and fats (6.1.1) | b) 4 marker PAHs |
| 506 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50 | a, b, c, d, j (plant materials) | b) 4 marker PAHs |
| 507 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | b) 10-50 | 6.1.1; 6.1.2; 6.1.3; 6.1.4; 6.1.7; 6.1.8 | c) 15+1 EU markers PAHs |
| 508 | a) Yes | b) no | a) yes | a) yes | e) >15 | b) 10-50 | k) All the matrices listed above | c) 15+1 EU markers PAHs |
| 509 | a) Yes | b) no | a) yes | a) yes | c) 4-8 | d) > 100 | 6.1.1,6.1.2,6.1.3,6.1.4,6.1.5,6.1.6,6.1.7,6.1.8 | c) 15+1 EU markers PAHs |
| 510 | a) Yes | b) no | a) yes | a) yes | b) 1-4 | c) 50-100 | a) Oils and fats (6.1.1) | c) 15+1 EU markers PAHs |

*Food categories as listed in Regulation (EC) No 1881/2006:*
a) Oils and fats (6.1.1)
b) Smoked meats and smoked meat products (6.1.2)
c) Muscle meat of smoked fish and smoked fishery products (6.1.3)
d) Muscle meat of fish (6.1.4)
e) Crustaceans, cephalopods, other than smoked (6.1.5)
f) Bivalve molluscs (6.1.6)
g) Processed cereal-based foods and baby foods for infants and young (6.1.7)
h) Infant formulae and follow-on formulae (6.1.8)
i) Dietary foods for special medical purposes (6.1.9)

**On the method applied**

- How did you prepare the sample?
- Which extraction method did you use?
- Which was the MAIN purification step of your method?
- Which was the instrumental detection method you applied?
- Please describe the analytical column used
- Did you encounter any problems during the analysis of the sample?

| Lab Code | Prepara-tion | Extraction | Purification | Detection | Column | Problem with analysis |
|---|---|---|---|---|---|---|
| 101 | b) No preparation | a) Saponification | d) Solvent partitioning | j) GC-MS | Varian PAH SELECT | Instrumental issues. |
| 102 | Saponificati on | e) cyclohexane extraction | c) Solid Phase Extraction (SPE) | j) GC-MS | DB-35ms, 30m, 0.25mm, 0.15µm | b) No |
| 103 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | C18, 5 µm, 4.6x250 mm | b) No |
| 104 | b) No preparation | e) liquid-liquid extraction | e) Other | j) GC-MS | SELECT PAH (30mx0.25mmx0.15um) | b) No |
| 105 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | PAH C18 5 um, 4.6x250 mm, 5 um (Waters P/N 186001265 | b) No |
| 106 | a) Dilution | e) liquid-liquid extraction with ecetonitrile/aceto ne | c) Solid Phase Extraction (SPE) | a) HPLC-FLD | C18 (specified for PAH's) 250 mm x 4,6 mm; part. size 5 um | b) No |
| 107 | b) No preparation | b) Pressurized liquid extraction | c) Solid Phase Extraction (SPE) | l) GC-MS/MS | Varian GC Capillary column, Select PAH - 15mm ID DF=0.10 mm | b) No |
| 108 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | k) GC-HRMS | varian select PAH, 30 m x 0.25 mm x 0.15 µm and DBr-MS, 60 m x 0.25 mm x 0.25 µm | Suppression on BaA/BaA-D12 and CHR/CHR-D12 signal on select PAH column |
| 110 | a) Dilution | e) liquid/liquid partitioning | c) Solid Phase Extraction (SPE) | j) GC-MS | Select PAH (30m×0,25mm×0,15µm) | b) No |
| 111 | b) No preparation | a) Saponification | d) Solvent partitioning | a) HPLC-FLD | LiChroCART 250-4, LiChrosper PAH (5 µm) | b) No |
| 112 | a) Dilution | e) Liquid/liquid Extraction | c) Solid Phase Extraction (SPE) | j) GC-MS | Restek Rxi-PAH 30m 0.25mm 0.10 um df | b) No |
| 113 | b) No preparation | a) Saponification | d) Solvent partitioning | j) GC-MS | 60m x 0.25mm x 0.25µ 5% phenyl polysiloxane | b) No |
| 114 | a) Dilution | d) No extraction | c) Solid Phase Extraction (SPE) | l) GC-MS/MS | SelectPAH 30 m × 0,25 mm × 0,15 µm | b) No |
| 115 | a) Dilution | d) No extraction | c) Solid Phase Extraction (SPE) | a) HPLC-FLD | RESTEK Pinneacle II 150*4,6*4 | b) No |
| 116 | b) No preparation | e) liquid/liquid partition | c) Solid Phase Extraction (SPE) | GC-MS (only for chrysene) and HPLC/FLD (for the rest PAHs) | SELECT PAH 30 m, 0.25 mm ID, 0.15 um f.t.; VYDAC 201 TP 54, 250 x 4.6 mm, 5 um | In Benzo(a)ant hracene peak |
| 117 | a) Dilution | e) liquid/liquid partition | b) Size-Exclusion Chromatography | j) GC-MS | 35% phenyl/65% methylpolysiloxane; 30m, 0.25 mm i.d., 0.25 µm film | b) No |
| 118 | a) Dilution | d) No extraction | c) Solid Phase Extraction (SPE) | l) GC-MS/MS | PAH Select column, 30m x 0,25mm x 0,15µm | b) No |
| 119 | a) Dilution | d) No extraction | c) Solid Phase Extraction (SPE) | l) GC-MS/MS | Agilent Select PAH (30 m x 0,25 mm x 0,15 µm) | b) No |
| 120 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | j) GC-MS | Zorbax Eclipse PAH 2.1x50 mm (1.8µm) | b) No |

| Lab Code | Prepara-tion | Extraction | Purification | Detection | Column | Problem with analysis |
|---|---|---|---|---|---|---|
| 121 | Addition of IS and weighing | d) No extraction | b) Size-Exclusion Chromatography | g) HPLC-MS/MS | Waters PAH C18, 5µm, 3x250mm | b) No |
| 123 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | Supelcosil LC-PAH, 25cm x 4.6mm, 5um | b) No |
| 124 | b) No preparation | b) Pressurized liquid extraction | c) Solid Phase Extraction (SPE) | c) HPLC-FLD-UV | Agilent Zorbax Eclipse Plus C18 3.5µm 100x4.6mm | b) No |
| 125 | a) Dilution | d) No extraction | a) (DACC) | a) HPLC-FLD | | b) No |
| 126 | b) No preparation | e) GPC | b) Size-Exclusion Chromatography | a) HPLC-FLD | specific PAH column C18, 4.6mmx 250 mm x5 um particle size. | cromatograp hic problems with the Chrysene |
| 501 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | | b) No |
| 503 | a) Dilution | e) shake sample with propanol | e) Other | c) HPLC-FLD-UV | 250 * 4,6 mm Chromspher 5 PAH, d = 7 µm | b) No |
| 504 | a) Dilution | d) No extraction | a) (DACC) | c) HPLC-FLD-UV | | b) No |
| 505 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | j) GC-MS | DB-EUPAH,20m,0.180mm 0.14µm | b) No |
| 506 | a) Dilution | a) Saponification | c) Solid Phase Extraction (SPE) | j) GC-MS | Varian Select PAH, 30m, 0,25mm, 0,15µm | little less material |
| 507 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | Pursuit 5 PAH, 250 x 4.6 mm | b) No |
| 508 | b) No preparation | a) Saponification | d) Solvent partitioning | l) GC-MS/MS | Select PAH (30mx250µmx0,15µm) | b) No |
| 509 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | 201TP 54 Grace 250 x 4,6 mm | b) No |
| 510 | a) Dilution | d) No extraction | b) Size-Exclusion Chromatography | a) HPLC-FLD | RP-C18, 5µm, 150 x 4.6mm | b) No |

## ANNEX 8: Data reported by participants

The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Limit of tolerance lines indicate the thresholds for satisfactory z-scores.

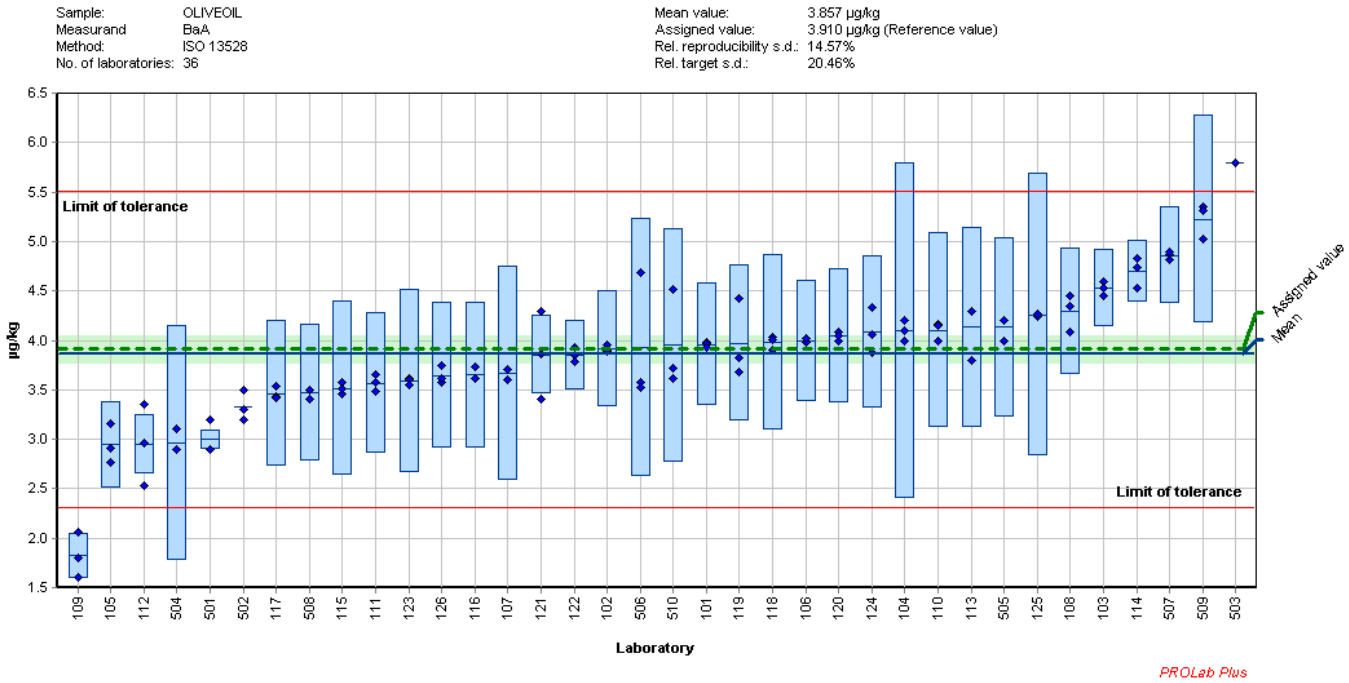
**Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) in the olive oil test material.** Assigned value is 3.91 µg/kg. The uncertainty refers to the final value.

| LCode | Measurand | Rep 1 | Rep 2 | Rep 3 | Final Value, µg/kg | Uncertainty, µg/kg | Technique |
|---|---|---|---|---|---|---|---|
| 101 | BaA | 3.98 | 3.97 | 3.93 | 3.93 | 0.62 | GC-MS |
| 102 | BaA | 3.89 | 3.96 | 3.9 | 3.92 | 0.59 | GC-MS |
| 103 | BaA | 4.6 | 4.45 | 4.53 | 4.53 | 0.39 | HPLC-FLD |
| 104 | BaA | 4 | 4.2 | 4.1 | 4.1 | 1.7 | GC-MS |
| 105 | BaA | 3.16 | 2.91 | 2.76 | 2.94 | 0.44 | HPLC-FLD |
| 106 | BaA | 3.98 | 3.98 | 4.02 | 3.99 | 0.61 | HPLC-FLD |
| 107 | BaA | 3.7 | 3.7 | 3.6 | 3.7 | 1.1 | GC-MS/MS |
| 108 | BaA | 4.09 | 4.45 | 4.35 | 4.3 | 0.64 | GC-HRMS |
| 109 | BaA | 1.6 | 2.06 | 1.8 | 1.82 | 0.23 | n.r. |
| 110 | BaA | 4 | 4.16 | 4.15 | 4.1 | 0.98 | GC-MS |
| 111 | BaA | 3.65 | 3.48 | 3.57 | 3.57 | 0.71 | HPLC-FLD |
| 112 | BaA | 2.53 | 2.96 | 3.36 | 2.95 | 0.3 | GC-MS |
| 113 | BaA | 3.8 | 4.3 | 4.3 | 4.1 | 1 | GC-MS |
| 114 | BaA | 4.83 | 4.74 | 4.53 | 4.7 | 0.31 | GC-MS/MS |
| 115 | BaA | 3.58 | 3.46 | 3.51 | 3.52 | 0.88 | HPLC-FLD |
| 116 | BaA | 3.61 | 3.62 | 3.73 | 3.66 | 0.74 | HPLC/FLD |
| 117 | BaA | 3.43 | 3.54 | 3.42 | 3.46 | 0.74 | GC-MS |
| 118 | BaA | 3.9 | 4.03 | 4.01 | 3.98 | 0.89 | GC-MS/MS |
| 119 | BaA | 3.82 | 3.68 | 4.42 | 3.97 | 0.79 | GC-MS/MS |
| 120 | BaA | 4.09 | 4 | 4.05 | 4.05 | 0.68 | GC-MS |
| 121 | BaA | 3.4 | 3.86 | 4.3 | 3.85 | 0.4 | HPLC-MS/MS |
| 122 | BaA | 3.85 | 3.78 | 3.93 | 3.86 | 0.35 | n.r. |
| 123 | BaA | 3.61 | 3.6 | 3.55 | 3.59 | 0.93 | HPLC-FLD |
| 124 | BaA | 4.33 | 4.06 | 3.87 | 4.08 | 0.77 | HPLC-FLD-UV |
| 125 | BaA | 4.246 | 4.265 | 4.27 | 4.26 | 1.431 | HPLC-FLD |
| 126 | BaA | 3.75 | 3.57 | 3.61 | 3.6 | 0.73 | HPLC-FLD |
| 501 | BaA | 3.2 | 2.9 | 2.9 | 3 | 0.1 | HPLC-FLD |
| 502 | BaA | 3.3 | 3.5 | 3.2 | 3.3 | 0 | n.r. |
| 503 | BaA | 5.8 | 5.8 | 5.8 | 5.8 | 0 | HPLC-FLD-UV |
| 504 | BaA | 3.1 | 2.9 | 2.9 | 3 | 1.2 | HPLC-FLD-UV |
| 505 | BaA | 4.2 | 4.2 | 4 | 4.1 | 0.9 | GC-MS |
| 506 | BaA | 3.58 | 4.68 | 3.53 | 3.93 | 1.3 | GC-MS |
| 507 | BaA | 4.81 | 4.87 | 4.9 | 4.86 | 0.49 | HPLC-FLD |
| 508 | BaA | 3.5 | 3.5 | 3.4 | 3.5 | 0.7 | GC-MS/MS |
| 509 | BaA | 5.345 | 5.03 | 5.306 | 5.227 | 20 | HPLC-FLD |
| 510 | BaA | 4.52 | 3.72 | 3.62 | 3.95 | 1.18 | HPLC-FLD |

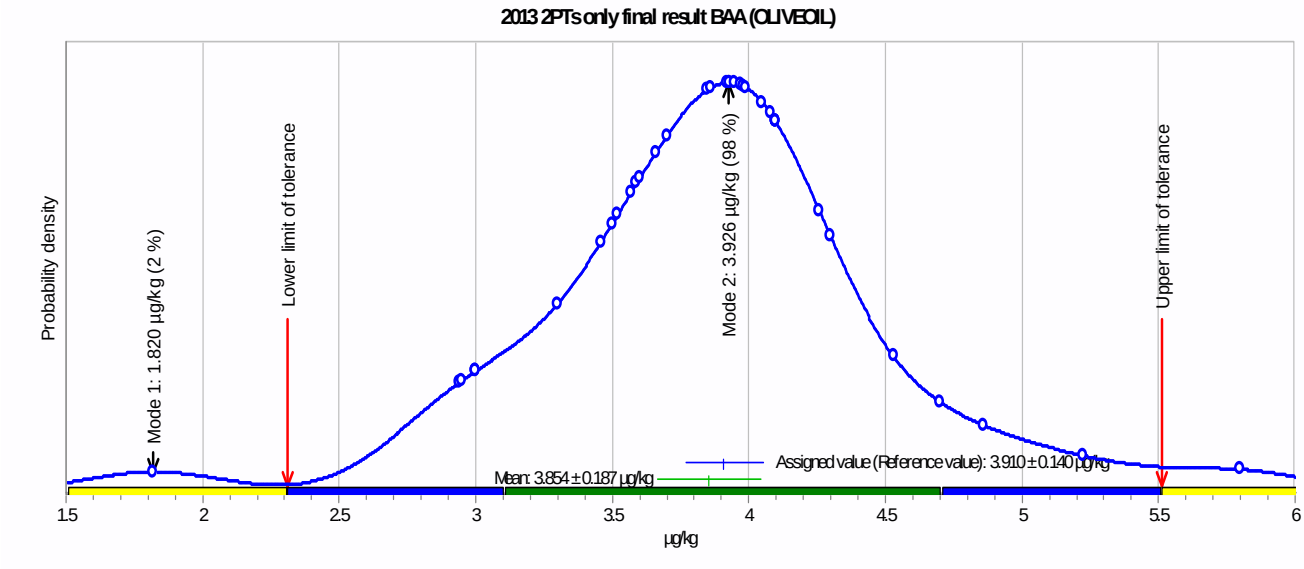
n.r.: not reported

**Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the olive oil test sample**

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, dotted line: assigned value, limit of tolerance: lower and upper limit of satisfactory z-score range




**Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content of the olive oil test sample**



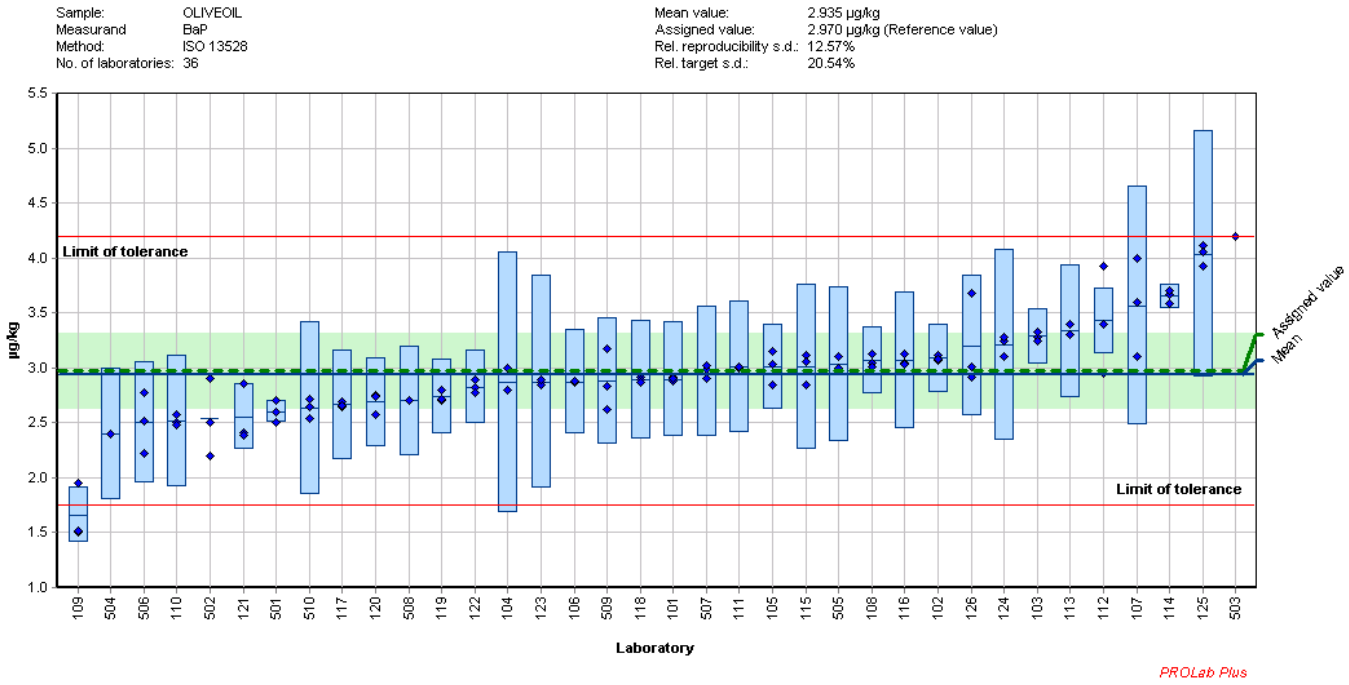
**Results, as reported by the participants, for the content of benz[*a*]pyrene (BAP) in the olive oil test material.** Assigned value is 2.97 µg/kg. The uncertainty refers to the final value.

| LCode | Measurand | Rep 1 | Rep 2 | Rep 3 | Final Value, µg/kg | Uncertainty, µg/kg | Technique |
|---|---|---|---|---|---|---|---|
| 101 | BaP | 2.91 | 2.88 | 2.9 | 2.9 | 0.52 | GC-MS |
| 102 | BaP | 3.07 | 3.11 | 3.08 | 3.09 | 0.31 | GC-MS |
| 103 | BaP | 3.28 | 3.25 | 3.33 | 3.29 | 0.25 | HPLC-FLD |
| 104 | BaP | 2.8 | 3 | 2.8 | 2.9 | 1.2 | GC-MS |
| 105 | BaP | 3.15 | 3.03 | 2.85 | 3.01 | 0.39 | HPLC-FLD |
| 106 | BaP | 2.87 | 2.87 | 2.88 | 2.87 | 0.47 | HPLC-FLD |
| 107 | BaP | 3.6 | 3.1 | 4 | 3.6 | 1.1 | GC-MS/MS |
| 108 | BaP | 3.13 | 3.05 | 3.01 | 3.01 | 0.3 | GC-HRMS |
| 109 | BaP | 1.51 | 1.95 | 1.52 | 1.66 | 0.25 | |
| 110 | BaP | 2.5 | 2.48 | 2.57 | 2.52 | 0.6 | GC-MS |
| 111 | BaP | 3.01 | 3 | 3.01 | 3.01 | 0.6 | HPLC-FLD |
| 112 | BaP | 2.95 | 3.4 | 3.93 | 3.43 | 0.3 | GC-MS |
| 113 | BaP | 3.3 | 3.3 | 3.4 | 3.3 | 0.6 | GC-MS |
| 114 | BaP | 3.67 | 3.7 | 3.59 | 3.65 | 0.11 | GC-MS/MS |
| 115 | BaP | 3.12 | 2.85 | 3.06 | 3.01 | 0.75 | HPLC-FLD |
| 116 | BaP | 3.04 | 3.03 | 3.13 | 3.07 | 0.62 | HPLC/FLD |
| 117 | BaP | 2.64 | 2.69 | 2.66 | 2.66 | 0.5 | GC-MS |
| 118 | BaP | 2.91 | 2.89 | 2.87 | 2.89 | 0.54 | GC-MS/MS |
| 119 | BaP | 2.8 | 2.7 | 2.72 | 2.74 | 0.34 | GC-MS/MS |
| 120 | BaP | 2.57 | 2.75 | 2.74 | 2.69 | 0.4 | GC-MS |
| 121 | BaP | 2.41 | 2.86 | 2.39 | 2.56 | 0.3 | HPLC-MS/MS |
| 122 | BaP | 2.89 | 2.82 | 2.77 | 2.83 | 0.33 | |
| 123 | BaP | 2.87 | 2.85 | 2.89 | 2.87 | 0.97 | HPLC-FLD |
| 124 | BaP | 3.25 | 3.28 | 3.1 | 3.21 | 0.87 | HPLC-FLD-UV |
| 125 | BaP | 3.93 | 4.118 | 4.054 | 4.034 | 1.121 | HPLC-FLD |
| 126 | BaP | 3.68 | 3.01 | 2.91 | 3.2 | 0.64 | HPLC-FLD |
| 501 | BaP | 2.7 | 2.6 | 2.5 | 2.6 | 0.1 | HPLC-FLD |
| 502 | BaP | 2.9 | 2.2 | 2.5 | 2.5 | 0 | |
| 503 | BaP | 4.2 | 4.2 | 4.2 | 4.2 | 0 | HPLC-FLD-UV |
| 504 | BaP | 2.4 | 2.4 | 2.4 | 2.4 | 0.6 | HPLC-FLD-UV |
| 505 | BaP | 3.1 | 3 | 3 | 3 | 0.7 | GC-MS |
| 506 | BaP | 2.22 | 2.77 | 2.52 | 2.5 | 0.55 | GC-MS |
| 507 | BaP | 2.9 | 2.99 | 3.02 | 2.97 | 0.59 | HPLC-FLD |
| 508 | BaP | 2.7 | 2.7 | 2.7 | 2.7 | 0.5 | GC-MS/MS |
| 509 | BaP | 3.177 | 2.621 | 2.836 | 2.878 | 20 | HPLC-FLD |
| 510 | BaP | 2.72 | 2.54 | 2.64 | 2.63 | 0.79 | HPLC-FLD |

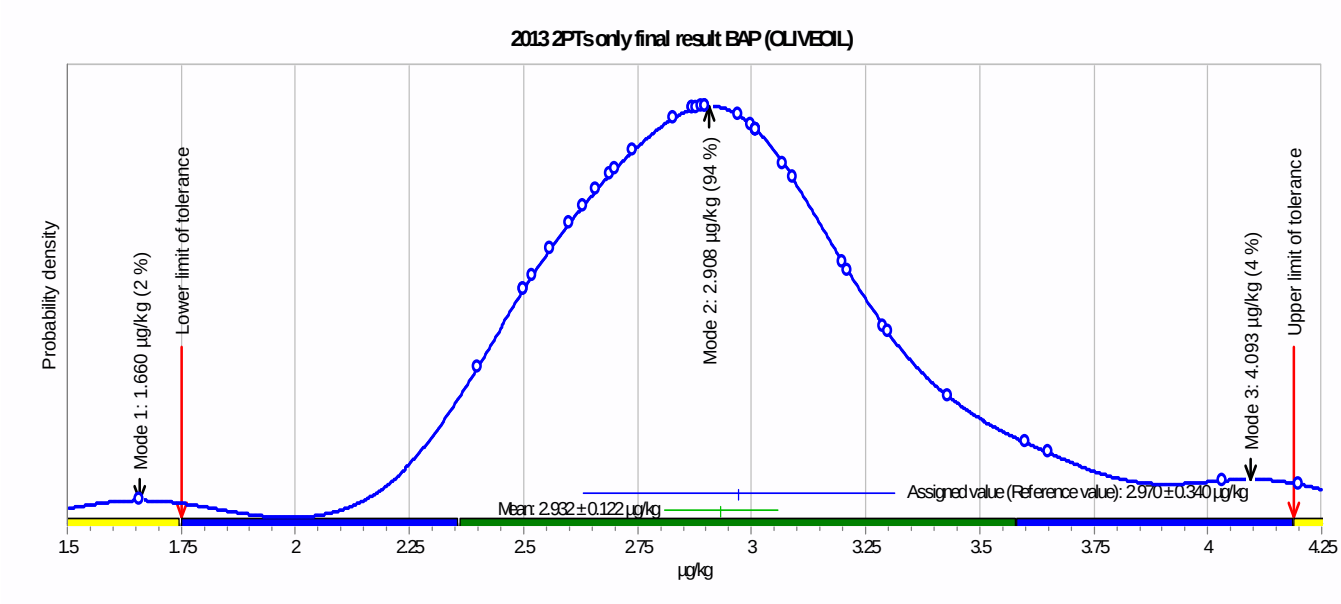
n.r.: not reported

## Distribution of individual results of replicate determinations reported for the benzo[*a*]pyrene (BAP) content of the olive oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, dotted line: assigned value, limit of tolerance: lower and upper limit of satisfactory z-score range




## Kernel density plot of the reported values for proficiency assessment for the benzo[*a*]pyrene (BAP) content of the olive oil test sample



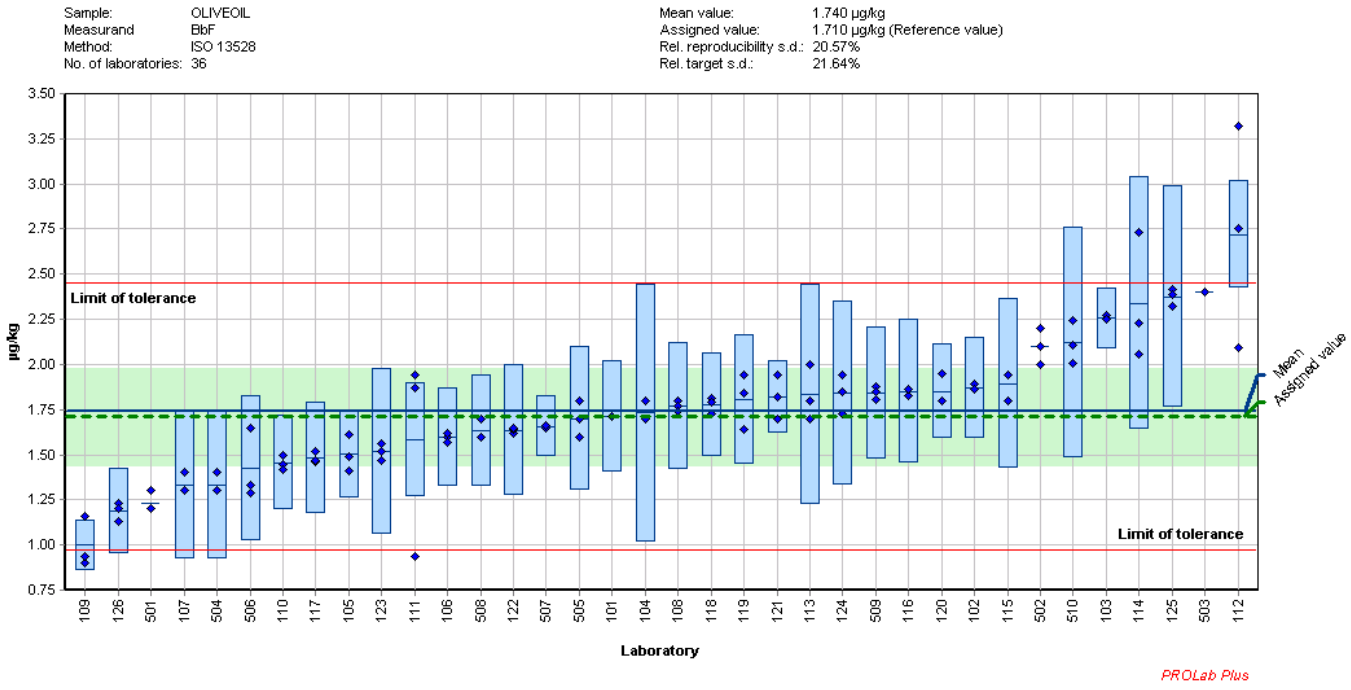
**Results, as reported by the participants, for the content of benz[*b*]fluorantene (BBF) in the olive oil test material.** Assigned value is 1.71 µg/kg. The uncertainty refers to the final value.

| LCode | Measurand | Rep 1 | Rep 2 | Rep 3 | Final Value, µg/kg | Uncertainty, µg/kg | Technique |
|---|---|---|---|---|---|---|---|
| 101 | BbF | 1.71 | 1.71 | 1.71 | 1.71 | 0.31 | GC-MS |
| 102 | BbF | 1.89 | 1.86 | 1.86 | 1.87 | 0.28 | GC-MS |
| 103 | BbF | 2.27 | 2.25 | 2.25 | 2.26 | 0.17 | HPLC-FLD |
| 104 | BbF | 1.7 | 1.8 | 1.7 | 1.7 | 0.7 | GC-MS |
| 105 | BbF | 1.61 | 1.41 | 1.49 | 1.5 | 0.24 | HPLC-FLD |
| 106 | BbF | 1.6 | 1.57 | 1.62 | 1.59 | 0.27 | HPLC-FLD |
| 107 | BbF | 1.4 | 1.3 | 1.3 | 1.3 | 0.4 | GC-MS/MS |
| 108 | BbF | 1.8 | 1.77 | 1.74 | 1.77 | 0.35 | GC-HRMS |
| 109 | BbF | 0.9 | 1.16 | 0.94 | 1 | 0.14 | |
| 110 | BbF | 1.45 | 1.5 | 1.42 | 1.46 | 0.26 | GC-MS |
| 111 | BbF | 1.87 | 1.94 | 0.94 | 1.92 | 0.38 | HPLC-FLD |
| 112 | BbF | 2.09 | 2.75 | 3.32 | 2.72 | 0.3 | GC-MS |
| 113 | BbF | 2 | 1.8 | 1.7 | 1.8 | 0.6 | GC-MS |
| 114 | BbF | 2.06 | 2.23 | 2.73 | 2.34 | 0.7 | GC-MS/MS |
| 115 | BbF | 1.94 | 1.8 | 1.94 | 1.89 | 0.47 | HPLC-FLD |
| 116 | BbF | 1.86 | 1.83 | 1.86 | 1.85 | 0.4 | HPLC/FLD |
| 117 | BbF | 1.46 | 1.52 | 1.47 | 1.48 | 0.31 | GC-MS |
| 118 | BbF | 1.73 | 1.81 | 1.79 | 1.78 | 0.29 | GC-MS/MS |
| 119 | BbF | 1.64 | 1.84 | 1.94 | 1.81 | 0.36 | GC-MS/MS |
| 120 | BbF | 1.8 | 1.95 | 1.8 | 1.85 | 0.26 | GC-MS |
| 121 | BbF | 1.94 | 1.82 | 1.7 | 1.81 | 0.2 | HPLC-MS/MS |
| 122 | BbF | 1.62 | 1.64 | 1.65 | 1.63 | 0.36 | |
| 123 | BbF | 1.47 | 1.56 | 1.52 | 1.52 | 0.46 | HPLC-FLD |
| 124 | BbF | 1.85 | 1.94 | 1.73 | 1.84 | 0.51 | HPLC-FLD-UV |
| 125 | BbF | 2.322 | 2.419 | 2.385 | 2.375 | 0.613 | HPLC-FLD |
| 126 | BbF | 1.13 | 1.23 | 1.2 | 1.2 | 0.24 | HPLC-FLD |
| 501 | BbF | 1.3 | 1.2 | 1.2 | 1.3 | 0 | HPLC-FLD |
| 502 | BbF | 2 | 2.1 | 2.2 | 2.1 | 0 | |
| 503 | BbF | 2.4 | 2.4 | 2.4 | 2.4 | 0 | HPLC-FLD-UV |
| 504 | BbF | 1.4 | 1.3 | 1.3 | 1.3 | 0.4 | HPLC-FLD-UV |
| 505 | BbF | 1.8 | 1.7 | 1.6 | 1.7 | 0.4 | GC-MS |
| 506 | BbF | 1.33 | 1.65 | 1.29 | 1.42 | 0.4 | GC-MS |
| 507 | BbF | 1.65 | 1.66 | 1.66 | 1.66 | 0.17 | HPLC-FLD |
| 508 | BbF | 1.6 | 1.6 | 1.7 | 1.6 | 0.3 | GC-MS/MS |
| 509 | BbF | 1.807 | 1.874 | 1.845 | 1.842 | 20 | HPLC-FLD |
| 510 | BbF | 2.24 | 2.01 | 2.11 | 2.12 | 0.64 | HPLC-FLD |

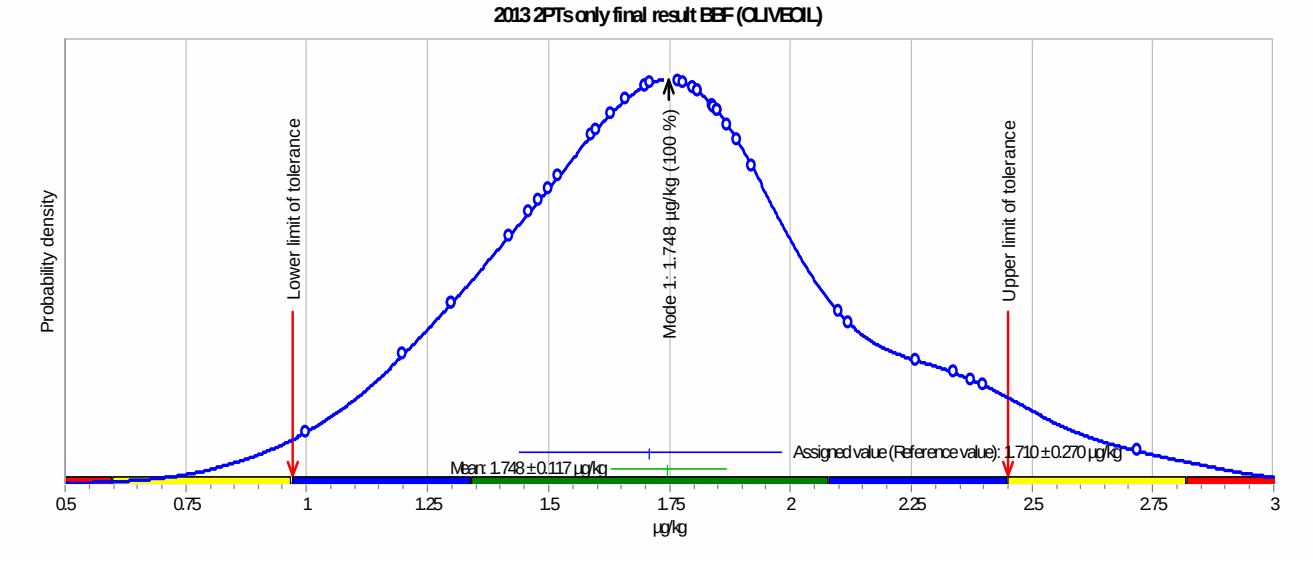
n.r.: not reported

## Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the olive oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, dotted line: assigned value, limit of tolerance: lower and upper limit of satisfactory z-score range




## Kernel density plot of the reported values for proficiency assessment for the benzo[*b*]fluoranthene (BBF) content of the olive oil test sample



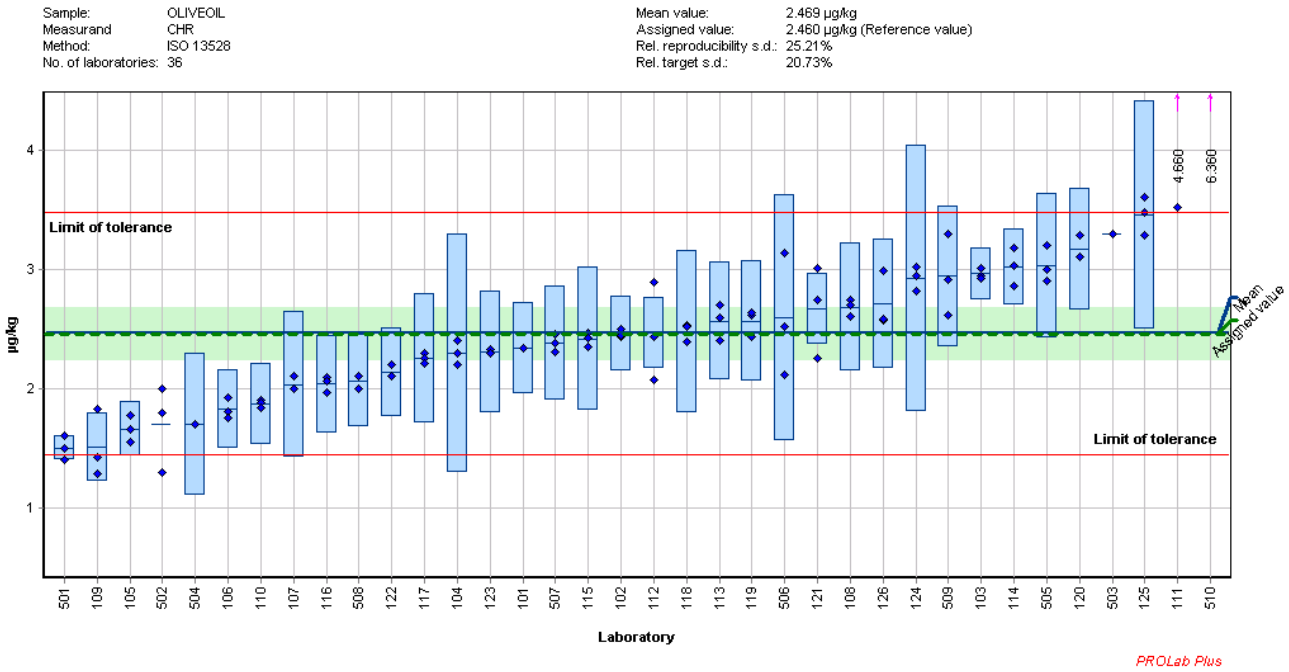
**Results, as reported by the participants, for the content of chrysene (CHR) in the olive oil test material.** Assigned value is 2.46 µg/kg. The uncertainty refers to the final value.

| LCode | Measurand | Rep 1 | Rep 2 | Rep 3 | Final Value, µg/kg | Uncertainty, µg/kg | Technique |
|---|---|---|---|---|---|---|---|
| 101 | CHR | 2.34 | 2.34 | 2.34 | 2.34 | 0.38 | GC-MS |
| 102 | CHR | 2.5 | 2.44 | 2.45 | 2.46 | 0.31 | GC-MS |
| 103 | CHR | 3.01 | 2.95 | 2.93 | 2.96 | 0.22 | HPLC-FLD |
| 104 | CHR | 2.2 | 2.4 | 2.3 | 2.3 | 1 | GC-MS |
| 105 | CHR | 1.77 | 1.55 | 1.66 | 1.66 | 0.23 | HPLC-FLD |
| 106 | CHR | 1.81 | 1.75 | 1.92 | 1.83 | 0.33 | HPLC-FLD |
| 107 | CHR | 2.1 | 2 | 2 | 2 | 0.6 | GC-MS/MS |
| 108 | CHR | 2.74 | 2.7 | 2.61 | 2.68 | 0.54 | GC-HRMS |
| 109 | CHR | 1.42 | 1.83 | 1.28 | 1.5 | 0.29 | |
| 110 | CHR | 1.9 | 1.88 | 1.84 | 1.87 | 0.34 | GC-MS |
| 111 | CHR | 5.78 | 4.68 | 3.52 | 4.66 | 0.94 | HPLC-FLD |
| 112 | CHR | 2.07 | 2.44 | 2.89 | 2.47 | 0.3 | GC-MS |
| 113 | CHR | 2.4 | 2.6 | 2.7 | 2.6 | 0.5 | GC-MS |
| 114 | CHR | 3.03 | 2.86 | 3.18 | 3.02 | 0.32 | GC-MS/MS |
| 115 | CHR | 2.47 | 2.35 | 2.43 | 2.42 | 0.6 | HPLC-FLD |
| 116 | CHR | 1.97 | 2.09 | 2.06 | 2.04 | 0.41 | GC-MS |
| 117 | CHR | 2.3 | 2.25 | 2.21 | 2.25 | 0.54 | GC-MS |
| 118 | CHR | 2.53 | 2.39 | 2.52 | 2.48 | 0.68 | GC-MS/MS |
| 119 | CHR | 2.44 | 2.62 | 2.64 | 2.57 | 0.51 | GC-MS/MS |
| 120 | CHR | 3.11 | 3.11 | 3.29 | 3.17 | 0.51 | GC-MS |
| 121 | CHR | 2.74 | 3.01 | 2.25 | 2.67 | 0.3 | HPLC-MS/MS |
| 122 | CHR | 2.1 | 2.11 | 2.2 | 2.14 | 0.37 | |
| 123 | CHR | 2.33 | 2.3 | 2.3 | 2.31 | 0.51 | HPLC-FLD |
| 124 | CHR | 3.02 | 2.82 | 2.95 | 2.93 | 1.12 | HPLC-FLD-UV |
| 125 | CHR | 3.484 | 3.283 | 3.603 | 3.457 | 0.957 | HPLC-FLD |
| 126 | CHR | 2.57 | 2.99 | 2.58 | 2.7 | 0.54 | HPLC-FLD |
| 501 | CHR | 1.6 | 1.5 | 1.4 | 1.5 | 0.1 | HPLC-FLD |
| 502 | CHR | 1.8 | 1.3 | 2 | 1.7 | 0 | |
| 503 | CHR | 3.3 | 3.3 | 3.3 | 3.3 | 0 | HPLC-FLD-UV |
| 504 | CHR | 1.7 | 1.7 | 1.7 | 1.7 | 0.6 | HPLC-FLD-UV |
| 505 | CHR | 3.2 | 3 | 2.9 | 3 | 0.6 | GC-MS |
| 506 | CHR | 2.12 | 3.14 | 2.52 | 2.59 | 1.03 | GC-MS |
| 507 | CHR | 2.46 | 2.31 | 2.38 | 2.38 | 0.48 | HPLC-FLD |
| 508 | CHR | 2.1 | 2 | 2.1 | 2.1 | 0.4 | GC-MS/MS |
| 509 | CHR | 2.62 | 2.92 | 3.293 | 2.944 | 20 | HPLC-FLD |
| 510 | CHR | 5.74 | 6.64 | 6.7 | 6.36 | 1.9 | HPLC-FLD |

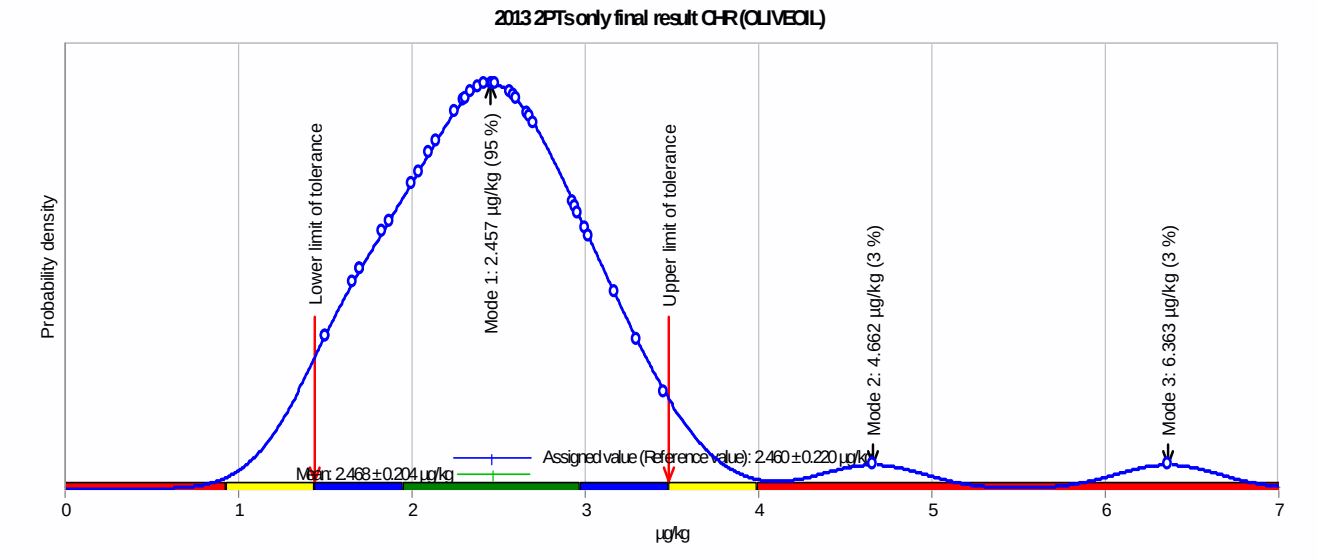
n.r.: not reported

**Distribution of individual results of replicate determinations of chrysene (CHR) in the olive oil test sample.**

*blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, dotted line: assigned value, limit of tolerance: lower and upper limit of satisfactory z-score range*




**Kernel density plot of the reported values for proficiency assessment for the chrysene (CHR) content of the olive oil test sample**



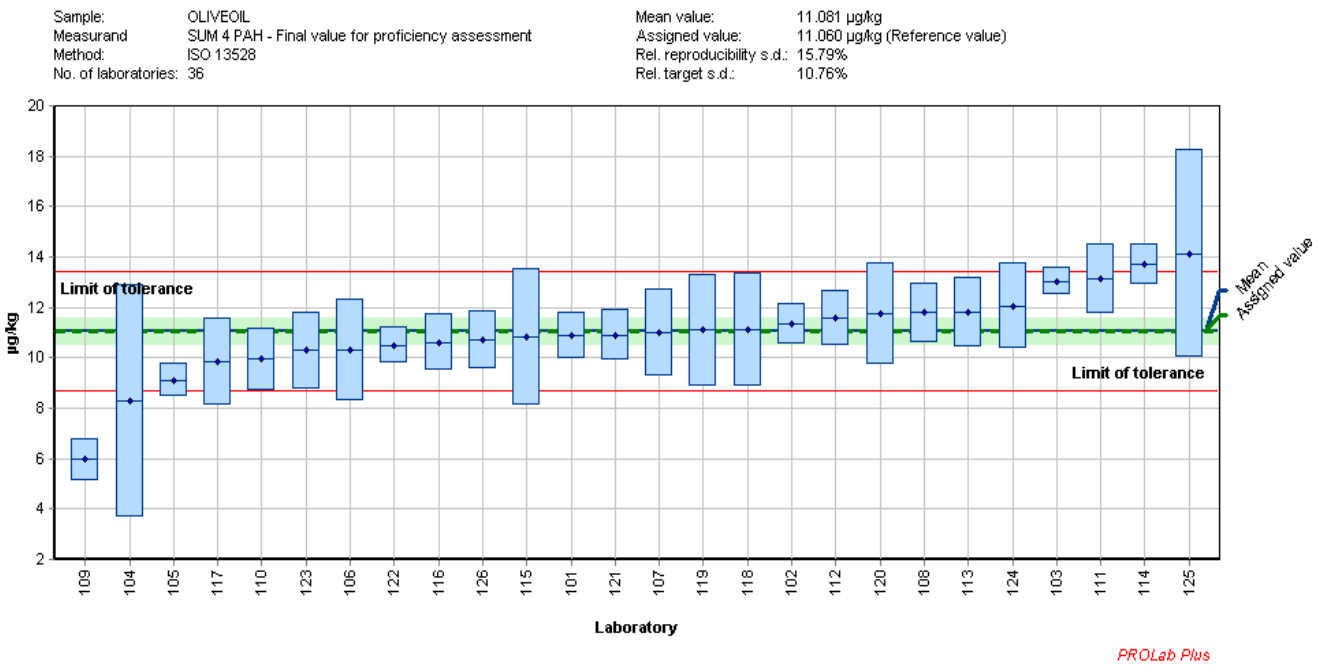
**Results, as reported by the participants, for the content of sum of the marker PAHs (SUM4PAH) in the olive oil test material.** Assigned value is 11.06 µg/kg. The uncertainty refers to the final value.

| LCode | Measurand | Final Value, µg/kg | Uncertainty, µg/kg | Technique |
|---|---|---|---|---|
| 101 | SUM 4 PAH | 10.88 | 0.95 | GC-MS |
| 102 | SUM 4 PAH | 11.34 | 0.79 | GC-MS |
| 103 | SUM 4 PAH | 13.04 | 0.54 | HPLC-FLD |
| 104 | SUM 4 PAH | 8.3 | 4.6 | GC-MS |
| 105 | SUM 4 PAH | 9.12 | 0.68 | HPLC-FLD |
| 106 | SUM 4 PAH | 10.32 | 2.01 | HPLC-FLD |
| 107 | SUM 4 PAH | 11 | 1.7 | GC-MS/MS |
| 108 | SUM 4 PAH | 11.8 | 1.18 | GC-HRMS |
| 109 | SUM 4 PAH | 5.98 | 0.84 | |
| 110 | SUM 4 PAH | 9.95 | 1.23 | GC-MS |
| 111 | SUM 4 PAH | 13.15 | 1.38 | HPLC-FLD |
| 112 | SUM 4 PAH | 11.57 | 1.1 | GC-MS |
| 113 | SUM 4 PAH | 11.8 | 1.4 | GC-MS |
| 114 | SUM 4 PAH | 13.72 | 0.8 | GC-MS/MS |
| 115 | SUM 4 PAH | 10.8 | 2.71 | HPLC-FLD |
| 116 | SUM 4 PAH | 10.62 | 1.12 | GC-MS (only CHR) HPLC/FLD |
| 117 | SUM 4 PAH | 9.86 | 1.73 | GC-MS |
| 118 | SUM 4 PAH | 11.13 | 2.24 | GC-MS/MS |
| 119 | SUM 4 PAH | 11.09 | 2.22 | GC-MS/MS |
| 120 | SUM 4 PAH | 11.75 | 2 | GC-MS |
| 121 | SUM 4 PAH | 10.9 | 1 | HPLC-MS/MS |
| 122 | SUM 4 PAH | 10.5 | 0.71 | |
| 123 | SUM 4 PAH | 10.29 | 1.51 | HPLC-FLD |
| 124 | SUM 4 PAH | 12.06 | 1.69 | HPLC-FLD-UV |
| 125 | SUM 4 PAH | 14.127 | 4.123 | HPLC-FLD |
| 126 | SUM 4 PAH | 10.7 | 1.14 | HPLC-FLD |
| 501 | SUM 4 PAH | 8.4 | 0.5 | HPLC-FLD |
| 502 | SUM 4 PAH | 9.6 | 0 | |
| 503 | SUM 4 PAH | 15.7 | 0 | HPLC-FLD-UV |
| 504 | SUM 4 PAH | 8.4 | 2.7 | HPLC-FLD-UV |
| 505 | SUM 4 PAH | 11.9 | 1.3 | GC-MS |
| 506 | SUM 4 PAH | 10.44 | 1.71 | GC-MS |
| 507 | SUM 4 PAH | 11.87 | 2.37 | HPLC-FLD |
| 508 | SUM 4 PAH | 9.9 | 2 | GC-MS/MS |
| 509 | SUM 4 PAH | 12.891 | 20 | HPLC-FLD |
| 510 | SUM 4 PAH | 15.07 | 5 | HPLC-FLD |

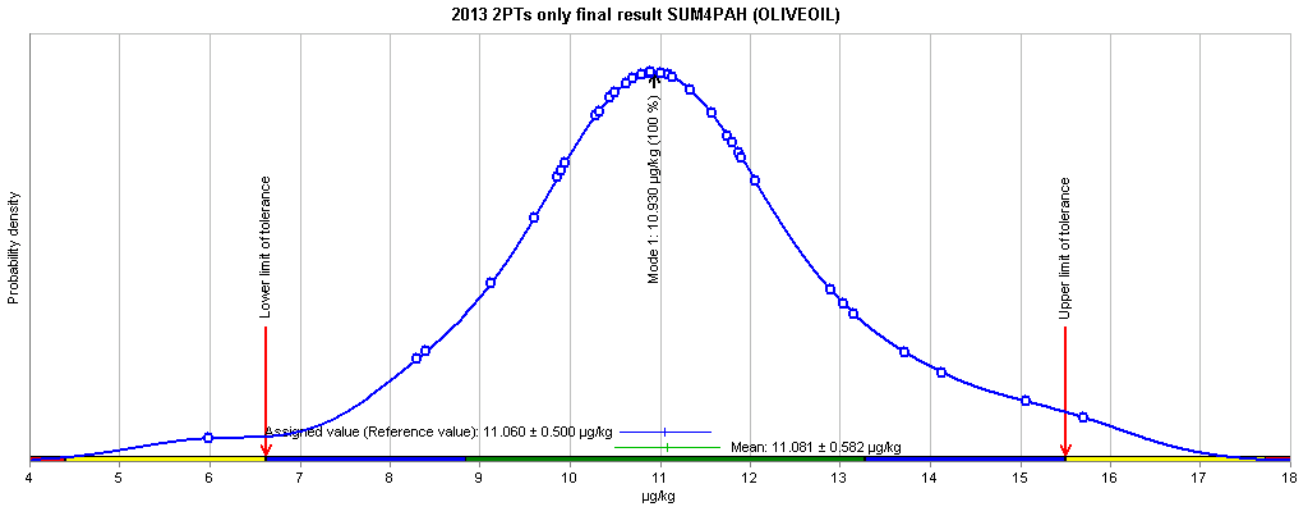
n.r.: not reported

**Distribution of individual results of replicate determinations of the sum of the contents of the four marker PAHs in the olive oil test sample.**

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, dotted line: assigned value, limit of tolerance: lower and upper limit of satisfactory z-score range

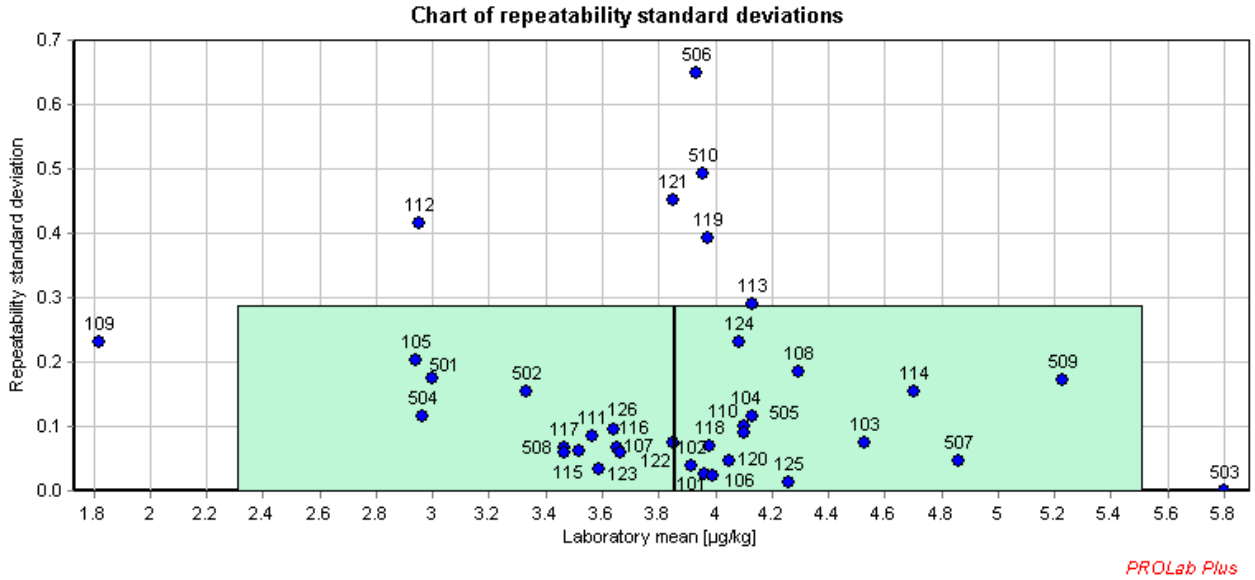



**Kernel density plot of the reported values for proficiency assessment for the SUM of 4 PAH content of the olive oil test sample**

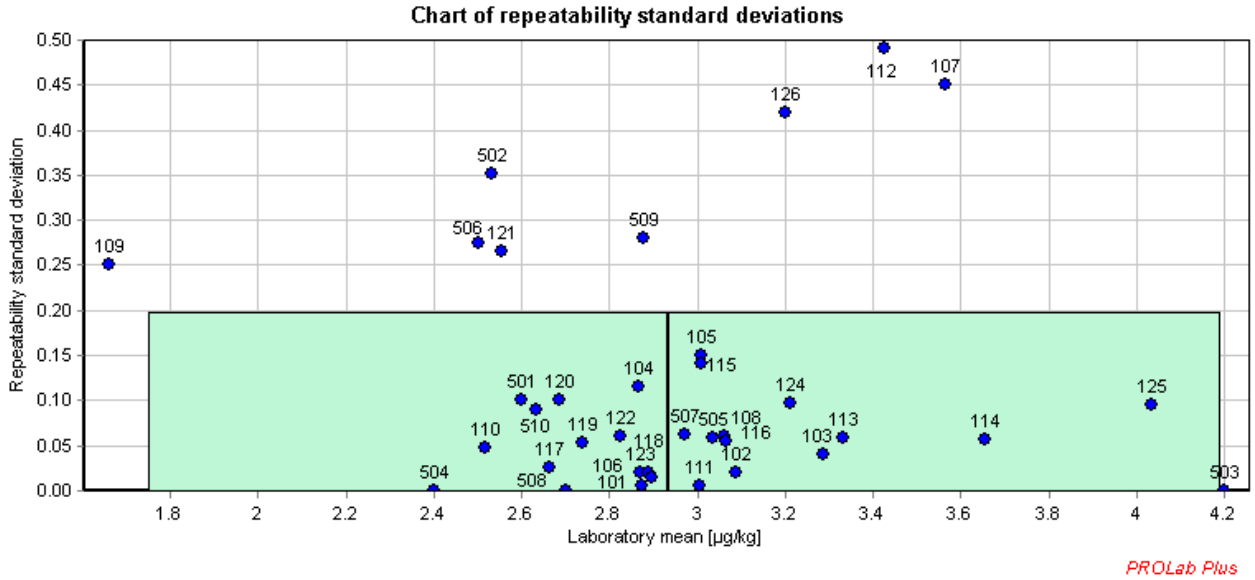


## ANNEX 9: Laboratory means and repeatability standard deviation

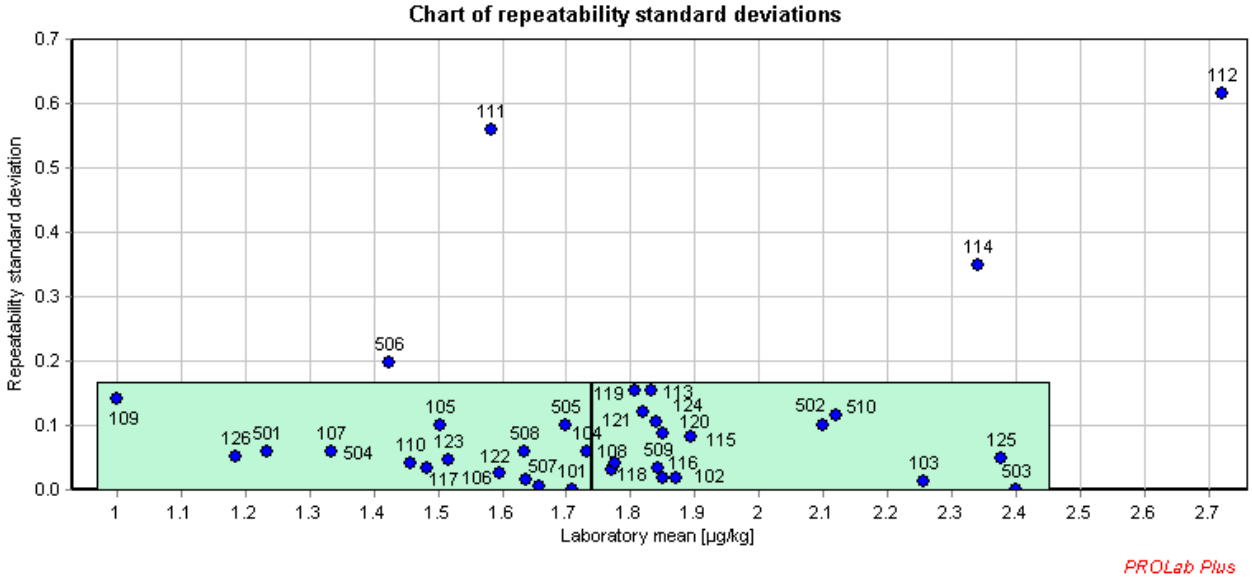
### Lab means and repeatability standard deviation for the determination of BAA in the olive oil test material



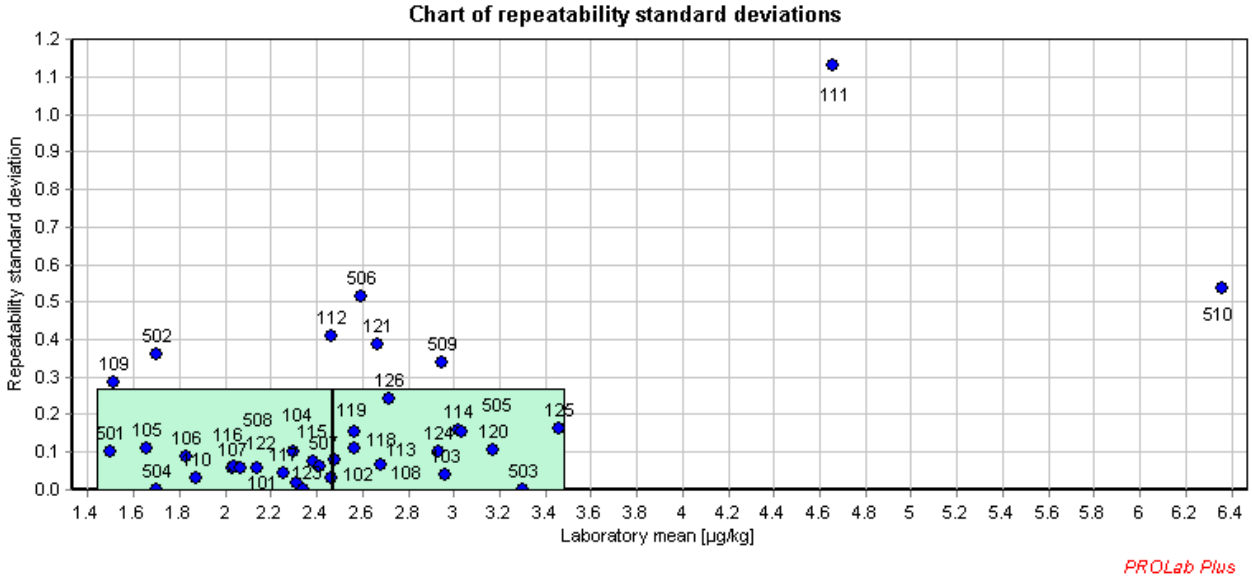

### Lab means and repeatability standard deviation for the determination of BAP in the olive oil test material



**Lab means and repeatability standard deviation for the determination of BBF in the olive oil test material**




**Lab means and repeatability standard deviation for the determination of CHR in the olive oil test material**



European Commission
EUR 26401 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: Report on the 13th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons - Four marker PAHs in spiked olive oil

Authors: Stefanka Bratinova, Zuzana Zelinkova, Lubomir Karasek and Thomas Wenzl

Luxembourg: Publications Office of the European Union

2013 – 58 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424 (online)

ISBN 978-92-79-34940-9

doi: 10.2787/84377

Abstract

The proficiency test here reported concerned the determination of the four marker polycyclic aromatic hydrocarbons (PAHs) in an olive oil test sample: benz[a]anthacene, benzo[a]pyrene, benzo[b]fluoranthene, and chrysene. Participants to these PT were National Reference Laboratories for PAHs (NRLs-PAHs) and EU official food control laboratories. The number of participants was 36. The PT was organised according to ISO Standard 17043:2010.

The test material used was olive oil spiked with the target PAHs. Participants also received a solution of the PAHs either in an organic solvent for checking their instrument calibration.

The results from participants were rated with z-scores and zeta-scores. About 94 % and 88 % of the results reported by NRLs and OCLs respectively were attributed with z-scores with an absolute value of below two, which is the threshold for satisfactory performance. The zeta-score ratings were worse, which indicates problems in the estimation of reliable measurement uncertainty values.

LA-NA-26401-EN-N

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ISBN 978-92-79-34940-9